CeMn\(_{1-x}\)O\(_2\) CATALYSTS SUPPORTED OVER γ-Al\(_2\)O\(_3\) PREPARED BY MODIFIED REDOX-COPRECIPITATION METHODS FOR n-HEXANE COMBUSTION

Jesus Rojas Quispe\(^a\), Romulo Cruz\(^b\), Rosario Sun Kou\(^a\) and Gino Picasso\(^a,\ast\)

\(^a\)Laboratory of Physical Chemistry Research, Faculty of Sciences, National University of Engineering, Tupac Amaru 210 Av., Rimac, Lima, Peru

\(^b\)Department of Sciences, Section Chemistry, Pontifical Catholic University of Peru, Av. Universitaria 1801, San-Miguel, Lima 32, Peru

Received on 24/06/2019; accepted on 14/01/2020; published online on 31/03/2020

A series of Ce\(_{x}\)Mn\(_{1-x}\)O\(_2\) catalysts supported on γ-alumina with various molar concentrations of Ce (\(x\), from 0 to 0.90) was synthesized by coprecipitation, applying two different precipitating agents, namely, sodium hydroxide (method 1) and sodium carbonate (method 2), with the use of sodium permanganate as a redox agent for precipitation. XRD profiles of the supported samples revealed the predominant abundance of a typical fluorite crystalline structure. TPR thermograms of supported samples were displaced towards lower temperatures with increasing Mn concentration, in contrast with the bulk samples. The supported Ce-Mn samples exhibited a greater performance in n-hexane elimination than did the corresponding simple oxides. The sample Ce\(_{0.33}\)Mn\(_{0.67}\)O\(_2\), obtained by method 2 presented the best activity, probably due to the enrichment of Ce\(^{4+}\), Mn\(^{4+}\) and Mn\(^{3+}\) surface species, an excess of superficial oxygen species and an easy reducibility as well as the lowest apparent activation energy.

Keywords: VOC; n-hexane; Ce-Mn; modified-precipitation; alumina.

INTRODUCTION

The world is increasingly aware of climate change and global warming, and the signatories of the twenty-first session of the Conference of the Parties (COP 2015, or the “Paris Accord”) have committed to intensify efforts to control carbon dioxide emissions. These reductions in emissions should limit a global temperature increase this century to less than two degrees above preindustrial levels. However, while important, carbon dioxide emissions are not the only large-scale pollution problem resulting from human activity. Volatile organic compounds (VOCs) form a group of chemicals responsible for photochemical smog, and many of them are known to be carcinogenic and teratogenic. Increasing regulations to control VOC levels, especially in work and home environments, demand the best technologies to control their release. Specifically promising is catalytic technology that allows VOCs to be eliminated at temperatures much lower than incineration combustion, making the formation of nitrogen oxides negligible.

The application of noble metals as catalysts in VOC combustion is usually limited by their high cost, scarcity and sensitivity at high temperatures. Metal oxides are promising alternatives due to their high activity and resistance to poisoning. In particular, the manganese oxides have been well studied in VOC combustion due to the chemical characteristic of manganese to the structure of multivalent oxides and their important ability to collect bulk oxygen. The formation of MnO\(_2\) species has shown high performance in the total combustion of different model organic molecules including α-xylene,\(^{2}\) methane,\(^{2}\) ethyl methyl ketone,\(^{2}\) 1,2-dichlorobenzene,\(^{2}\) n-hexane,\(^{2}\) toluene\(^{2}\) and ethanol,\(^{2}\) among others.

n-Hexane is a solvent commonly used in the chemical industry, but its application in the manufacturing of drugs has been restrained due to its ongoing toxicity. OSHA\(^{15}\) and NIOSH\(^{16}\) have regulated its emission to the atmosphere as a hazard, setting an exposure limit of 500 ppm for 8 h. In previous works, some catalysts based on CeMnO\(_2\) and CeZrO\(_2\) were prepared in a membrane configuration and in a packed-bed reactor with bulk samples for the elimination of n-hexane. The catalytic tests revealed a strong influence of the Mn\(^{4+}\) and Ce\(^{4+}\) species over the surface, which had the ability of storing surface oxygen through redox reactions following a Langmuir-Hinshelwood mechanism. While redox processes clearly played a substantial role in the catalytic performance, some questions related to the preparation variables and their influence on the formation of the active phase require deeper discussion as is suggested by some authors.\(^{20}\) With this aim, some factors were taken into consideration in this work, namely, the dispersion effect using a conventional γ-alumina support and the effect of preparation variables proposed via modifying precipitation agents and calcination conditions as well as their influence on the catalytic behavior of alumina-supported Ce-Mn oxides in the abatement of n-hexane.

EXPERIMENTAL

Catalyst preparation

A series of Ce\(_{x}\)Mn\(_{1-x}\)O\(_2\) catalysts was synthesized modifying the relative molar concentration of cerium from \(x=0.33\) to 0.9 by coprecipitation using different precipitating agents and redox conditions. Prior to the preparation of the catalysts, the γ-Al\(_2\)O\(_3\) support (99.9%, SIGMA-ALDRICH) was heated to 135 °C in a closed balloon reactor under vacuum to eliminate any remaining water, which was verified by the differences in weights before and after the thermal treatment. Moreover, the alumina-supported simple oxides were prepared for \(x=0\) (CeO\(_2\)) and for \(x=1\) (MnO\(_2\)) following each method of preparation, which were the following:

Method 1

In method 1, the catalysts were prepared by suspension-coprecipitation with a redox reaction step using a solution of 0.2 mol L\(^{-1}\) NaOH (MERCK) as a precipitating agent. This solution was added at 0.5 mL min\(^{-1}\) to a beaker containing a suspension of
γ-Al2O3 with a 0.5 mol L⁻¹ solution of metalic precursors of a mixture of Ce and Mn nitrates and potassium permanganate with a molar ratio (m/m) of 5:3.2, respectively, at 60 °C under constant stirring to achieve a pH up to 10.5.21,22 The solid was aged for 2 h and washed 5 times using deionized water to avoid the presence of the remaining alkali ions. Finally, the solid was dried at 110 °C for 12 h and calcined for 6 h at 500 °C under air atmosphere (heating rate=5 °C/min). The mechanism of preparation corresponds to the mixed precipitation-redox route developed over the support γ-Al2O3:23

\[
\begin{align*}
\text{MnO}_4^- + 3e^- + 2H_2O & \rightarrow \text{MnO}_2 + 4OH^- \\
\text{Mn}^{2+} + 4OH^- & \rightarrow \text{MnO}_2 + 2e^- + 2H_2O \\
\text{Ce}^{3+} + 4OH^- & \rightarrow \text{CeO}_2 + e^- + 2H_2O
\end{align*}
\]

The mechanism of preparation corresponds to the mixed precipitation-redox route developed over the support γ-Al2O3.23

\[
\begin{align*}
3 \text{ mol MnVII} + 2 \text{ mol MnII} + \text{ mol CeIII} &= (\text{mol Mn} / \text{mol Ce}) (b) \\
\text{mol MnVII} + \text{ mol MnII} + \text{ mol CeIII} &= 1 (c)
\end{align*}
\]

The equations correspond to the (a) charge balance, (b) molar balance and (c) compositional balance of the catalyst.

**Method 2**

This method was similar to method 1, but using a solution of 0.2 mol L⁻¹ Na2CO3 as a precipitating agent,24,25 which was introduced to a solution of Ce and Mn nitrate precursors with potassium permanganate with the molar ratio of 5:3.2, respectively, at 50 °C, increasing the pH level to 10.5 under vigorous stirring. Then, the solid was aged for 2 h and washed until removal of Na⁺. The final solid was dried at 110 °C for 12 h, heated at a heating rate of 5 °C/min and finally calcined at 500 °C for 6 h in air. The mechanistic route of the process was the following:

\[
\begin{align*}
\text{MnO}_4^- + 3e^- + 2H_2O & \rightarrow \text{MnO}_2 + 4OH^- \\
\text{Mn}^{2+} + \text{CO}_3^{2-} & \rightarrow \text{MnCO}_3(s) \\
2\text{Ce}^{3+} + 3\text{CO}_3^{2-} & \rightarrow \text{Ce}_2(\text{CO}_3)_3(s) \\
(2\times) \text{Ce}_2(\text{CO}_3)_3(s) + (1-x) \text{MnCO}_3(s) & \rightarrow \text{Ce}_{1-x}\text{Mn}_x\text{O}_2(s) + \text{CO}_2(g)
\end{align*}
\]

Table 1 lists the alumina-supported mixed catalysts (CeMnₓOᵧ) prepared in this work. The mixed oxide supported catalysts were denoted as CMx-y, in which “x” is assigned to the nominal metallic ratio Ce/(Ce+Mn), and “y” indicates the method of preparation. The simple oxide supported samples were denoted as C-x or M-x, in which “x” corresponds to the nominal metallic ratio Ce/(Ce+Mn), and “y” indicates the method of preparation.

| Catalyst | Method of preparation | CeMn ratio | S_BET (m²/g) |
|----------|-----------------------|------------|--------------|
| **Comparative method** | | | |
| CM0.5-1 | 1 | 1 | 174 |
| CM0.5-2 | 2 | 1 | 182 |
| γ-Al2O3 | - | - | 170 |
| **Comparative Ce/(Ce+ Mn) ratio - Method 1** | | | |
| CM0.33-1 | 1 | 0.5 | 169 |
| CM0.5-1 | 1 | 1 | 174 |
| CM0.67-1 | 1 | 2 | 236 |
| CM0.9-1 | 1 | 9 | 211 |
| C-1 | 1 | - | 157 |
| M-1 | 1 | - | 124 |
| **Comparative Ce/(Ce+ Mn) ratio - Method 2** | | | |
| CM0.33-2 | 2 | 0.5 | 129 |
| CM0.5-2 | 2 | 1 | 182 |
| CM0.67-2 | 2 | 2 | 177 |
| C-2 | 2 | - | 168 |
| M-2 | 2 | - | 132 |

Table 1. Alumina-supported mixed catalysts based on CeMnₓOᵧ (40% metallic charge) prepared in this work

The crystal structures of the catalysts were studied by X-ray diffraction (XRD). The characterization was performed using a RIGAKU Miniflex diffractometer, whose operating parameters were as follows: 15 mA, 30 kV, Cu Kα radiation (λ = 1.5418 Å), Ni filter, and range of angle scanning from 5 to 80° (step size = 0.10° and step time = 2.5 s). The identification of the crystal phases was made by application of the PDF2 database from ICDD. The Scherrer equation was used to estimate the average crystallite sizes from the peak of the highest intensity in the diffractograms, and the Gauss function was used to fit the selected diffraction peaks.

The texture of the catalysts was analyzed by the technique of sorption of N₂, performed at liquid nitrogen temperature with a Micromeritics GEMINI VII-2390t system. Before the analysis, the catalysts were pretreated in a He stream at 250 °C for 2 h. The BET method and the t-plot procedure were applied to evaluate the total specific surface area and the microporous area of catalyst, respectively. The method of BJH (Barrett, Joyner, and Halenda) from the adsorption at a P/P₀ near 0.98 was used to measure the total pore volume as well as the pore size distribution and the mean pore size (using the desorption branch of the isotherm).

The redox properties of the catalysts were studied by temperature-programmed reduction (H₂-TPR) and temperature-programmed desorption of oxygen (O₂-TPD), performed with a MICROMERITICS CHEMISORB 2720 Pulse Chemisorption System. As a rule, the TPR tests were carried out in a U-tube quartz reactor in which 25 mg of the sample was deposited under a stream of 10% H₂/He and warmed from the room temperature to 900 °C at a heating rate of 10 °C min⁻¹. A standard quantity of Ag₂O was used to calibrate the H₂-consumption. The estimation of oxidation state of Mn has been made considering only the MnO as the oxide present at the end of all the TPR tests. The O₂-TPD tests were performed in a reactor using 100 mg of the sample pretreated with a helium purge (25 mL min⁻¹) for 30 minutes at 200 °C and followed by an injection of a flow of 10% O₂ in He (25 mL min⁻¹) for 30 minutes at 500 °C. Then, under a gas stream of 10% He in N₂, the catalysts were cooled to room temperature. Finally, another helium purge (25 mL min⁻¹) was performed to remove O₂ molecules, heating the furnace at a rate of 10 °C min⁻¹ from 30 °C to 850 °C. A thermal conductivity detector (TCD) was employed to quantify the loss of O₂.

The chemical surface analysis of samples was evaluated by X-ray photoelectron spectroscopy (XPS). The spectrometer used was VG 200 R with a 120 W-powered X-ray source of Al Kα1 (hv = 1486.6 eV). The XPS spectra were recorded on small Inox holders with a vacuum system, heating in the presence of a residual
pressure of $10^4$ mbar at 573 K for 5 h. Furthermore, the spectra were collected at 200 eV pass energy for survey spectra and 50 eV pass energy for narrow scans. Afterwards, the catalysts were introduced into the analysis chamber in which a residual pressure of $5.10^2$ mbar was inserted. High-resolution spectra of Ce 3d, Mn 2p, C 1s and O 1s and a survey spectrum were acquired for each catalyst, each with multiple scans in order to achieve good signal-to-noise ratios. The binding energies of Cu 2p3/2 (932.6 eV) and Au 4f7/2 (84.0 eV) were used as a calibration reference of the spectrometer. The binding energy of the C 1s signal of adventitious carbon at 284.8 eV was used to correct possible generated charge effects of spectra of the catalysts. The fitting of the experimental spectra with ±0.1 eV of precision of the binding energy values was achieved through a combination of Gaussian and Lorentzian lines (G/L = 90/10), subtracting the C 1s signal of adventitious carbon at 284.8 eV was used to correct possible generated charge effects of spectra of the catalysts. The characterization by H2-TPR analysis was applied to the alumina-supported mixed samples prepared by method 1 differ from those of method 2 because the majority phase is now monoclinic MnO2 (PDF2 # 39e1218) and cubic MnO2 (PDF2 # 73e1826) instead of tetragonal MnO2 (PDF2 # 24e0734), as has also been observed by some authors.26

Temperature programmed reduction (TPR)

The characterization by H2-TPR analysis was applied to the alumina-supported mixed oxides prepared by different methods. The support γ-AL2O3 presented a consumption of H2 at reduction temperatures over than 1000 °C; consequently, the reduction peaks observed in the H2-TPR thermograms are exclusively owing to
the reduction of the metallic species. In the profile corresponding to C-2 (40%) presented in Figure 3, two reduction peaks are depicted, at 516 °C and 690 °C, which are consistent with the reduction of nonstoichiometric superficial Ce\(^{4+}\) species (tetrahedrally coordinated with the oxygen atoms) and the reduction of Ce\(^{4+}\) to Ce\(^{3+}\) in the bulk phase, respectively.\(^{17}\) The first peak was shifted to the higher temperatures with respect to that observed in the bulk phase in previous work,\(^{14}\) probably due to the interaction with the \(\gamma\)-Al\(_2\)O\(_3\) support. The reduction of Ce\(^{4+}\) to Ce\(^{3+}\) (bulk) is typical of the fluorite crystalline structure,\(^{14}\) which confirms the XRD diffractograms, as already discussed.

The \(\text{H}_2\)-TPR profile of M-2 (40%) shown in Figure 3 exhibits three reduction peaks positioned at temperatures near 320, 360 and 443 °C, ascribed to the successive reduction steps from MnO\(_2\) to MnO as reported by some authors,\(^{27,28}\)

\[
\text{MnO}_2 \rightarrow \alpha\text{-Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}
\]  

As discussed in previous work,\(^{14}\) the stoichiometry of bulk manganese oxide calculated from the consumption of \(\text{H}_2\) of the corresponding profile in Figure 3 is in good agreement with the presence of Mn\(_2\)O\(_3\), Mn\(_3\)O\(_4\), and MnO\(_2\). In this case, the reduction temperatures were displaced towards higher temperatures than those observed in the bulk phase,\(^{14}\) which is compatible with the influence of the metal-support interactions. All these data are in good agreement with the XRD diffractograms of Figure 2.

The \(\text{H}_2\)-TPR thermograms of a series of catalysts CM0.5 (40%) prepared by methods 1 and 2 are presented in Figure 3. All the profiles are very similar, no matter the method of preparation, and exhibit one broad defined peak, situated at 240-250 °C, and a shoulder at 410-415 °C. According to some authors,\(^{29}\) the first peak could be assigned to the reduction of superficial Mn\(^{4+}\) species situated over Ce lattice positions, and the second peak could be attributed to the reduction of Mn\(^{3+}\) species. The profile of the CM0.5-2 (40%) differs from the others due to the presence of a broader peak at the first reduction temperature, probably due to the major consumption of \(\text{H}_2\), revealing an easier reducibility caused by the better positions of Mn\(^{4+}\) species over the surface. Moreover, in this sample, a minor peak situated at 411 °C confirmed that the Mn\(_2\)O\(_3\) particles are quickly transformed, remaining only as the Mn\(^{3+}\) species, exhibiting a broader peak, most likely owing to a much higher dispersion of the active phase.\(^{30}\)

The \(\text{H}_2\)-TPR thermograms of a series of catalysts CM0.5 (40%) prepared by methods 1 and 2 are presented in Figure 3. All the profiles are very similar, no matter the method of preparation, and exhibit one broad defined peak, situated at 240-250 °C, and a shoulder at 410-415 °C. According to some authors,\(^{29}\) the first peak could be assigned to the reduction of superficial Mn\(^{4+}\) species situated over Ce lattice positions, and the second peak could be attributed to the reduction of Mn\(^{3+}\) species. The profile of the CM0.5-2 (40%) differs from the others due to the presence of a broader peak at the first reduction temperature, probably due to the major consumption of \(\text{H}_2\), revealing an easier reducibility caused by the better positions of Mn\(^{4+}\) species over the surface. Moreover, in this sample, a minor peak situated at 411 °C confirmed that the Mn\(_2\)O\(_3\) particles are quickly transformed, remaining only as the Mn\(^{3+}\) species, exhibiting a broader peak, most likely owing to a much higher dispersion of the active phase.\(^{30}\)

The influence of metal composition on the reduction properties of the catalysts from method 2 (40%) is depicted in Figure 2S. The thermograms were shifted to lower temperatures with decreasing Ce/Mn ratio due to the enrichment in Mn. The higher area of the first peak in the TPR, corresponding to both CM0.5-2 and CM0.33-2, reveals the major consumption of \(\text{H}_2\) in relation to the predominant concentration of Mn\(^{4+}\) reduced to Mn\(^{3+}\) species. The best reducibility in the catalysts CM0.33-2 led to a better performance in the total oxidation of n-hexane, so it was studied in greater detail. The results of the O\(_2\)-TPD analysis (Figure 3S) showed that the labile species of oxygen are in the highest concentration in the mixed samples and that method 2 led to catalysts with a higher quantity of labile oxygen, which was desorbed at low temperatures.

X-ray photoelectron spectroscopy (XPS)

Table 3 shows the normalized absolute areas from the XPS spectrum (in CPS.eV) of a series of CM0.33 (40%) alumina-supported catalysts synthesized by methods 1, 2 as well as the corresponding catalysts prepared by method 2, CM-0.33-2 (30%), CM-0.33-2 (20%) and the simple oxides C-1 (40%), M-1 (40%), prepared by method 1. To determine the atomic percentages, the atomic ratios were normalized using the corresponding sensitivity factors.

The signals corresponding to the Mn 2p\(^{3/2}\) XPS spectrum
Ce<sub>α</sub>Mn<sub>1-α</sub>O<sub>2</sub> catalysts supported over γ-Al<sub>2</sub>O<sub>3</sub> prepared by modified redox-coprecipitation methods

(Figure 4) of a series of catalysts were deconvoluted by a fitting process after subtraction of the background, using XPS commercial software. The compounds MnO, ZnMn<sub>2</sub>O<sub>4</sub> and MgNiMnO<sub>4</sub> were used as references of the binding energies and FWHM values of the Mn<sup>2+</sup> (641.1 eV, 2 eV), Mn<sup>3+</sup> (641.9 eV, 2.7 eV) and Mn<sup>4+</sup> (644.0 eV, 4 eV).<sup>31-33</sup> The Mn 2p core level in pure MnO<sub>x</sub> (M-1, 40%) allowed finding a Mn cation distribution expressed as a percentage ratio [Mn<sup>2+</sup>]: [Mn<sup>3+</sup>]: [Mn<sup>4+</sup>] equal to 19.9: 53.8: 26.2, from which it was inferred that Mn<sup>3+</sup> and Mn<sup>4+</sup> were the majority species (Table 3). Similar results were obtained for the samples of a series of CM-0.33 catalysts prepared by different methods (Figure 4). As is observed, in the sample CM0.33-2, prepared by method 2, Mn<sup>4+</sup> species are in a greater proportion than in the samples prepared by method 1. Additionally, the low surface percentage of Mn over the support (Table 3) indicates a good dispersion of the active phase. In the case of the CM0.33 series catalysts prepared by method 2 and with different metallic loads, as is observed in Table 4, the total percentage of Mn<sup>4+</sup> and Mn<sup>3+</sup> increases as the metallic load increases.

The O 1s spectra of the mixed oxides (Figure 5) were deconvoluted into two contributions, namely, surface-adsorbed oxygen in the BE range of 531 to 531.6 eV, related to defect surface oxygen species such as O<sub>2</sub><sup>-</sup> or O<sup>-</sup> (usually denoted as O<sub>β</sub>), and the corresponding BE range of 528.9–530 eV, usually ascribed to lattice oxygen (O<sub>α</sub>). During the deconvolution of the different samples, the FWHM value was maintained constant in the range of ±0.1 eV. The O 1s spectrum of C-1 (40%) presented two maxima centered at 529.5 and 531.6 eV, attributed to lattice oxygen and surface oxygen, respectively; meanwhile, the O 1s core level of oxygen of M-1 (40%) was situated at 530.2 and 531.5 eV. For C-1 (40%), the percentage of superficial oxygen abundance was 82.2, and for M-1 (40%), 95.3.

According to Table 4, sample CM0.33-2 (40%) presented a higher relative enrichment of adsorbed oxygen (100%) than did the other analogous samples prepared by method 1 (82.1%) (Figure 5). This enrichment in surface oxygen in alumina-supported mixed samples of Ce-Mn is in accordance with the data discussed by Arena et al.,<sup>30</sup> in which the formation of very reactive electrophilic oxygen species was ascribed to the “Mn<sup>4+</sup>–O<sup>-</sup>” electron-transfer processes. Moreover, the increase in the metal load over the support from 20 to 40% had no significant effect on the percentage of surface oxygen, as is observed in Table 4 with the CM0.33 sample series prepared by method 2.

![Figure 4. Mn 2p3/2 XPS spectra: deconvoluted peaks of samples prepared by different methods of preparation. Peaks are centered at 641.1 eV (Mn<sup>2+</sup>), 641.9 eV (Mn<sup>3+</sup>) and 644 eV (Mn<sup>4+</sup>), a: M-1, b: CM0.33-1, c: CM0.33-2](image-url)
the percentage of Ce$^{4+}$ in all samples ranged from 81.6 to 86.5. Most likely, according to some authors, the content of Ce$^{3+}$ reported in this work is due to the reduction of Ce$^{4+}$ that takes place during the XPS analysis.

Catalytic activity of the catalysts in the combustion of n-hexane

The combustion of n-hexane performed without a catalyst indicated the absence of activity at the working temperatures. The following experimental variables were considered in all the catalytic tests: method of preparation, the metallic load of the active phase over the support and the composition of metal loading over the support.

Influence of the metallic load

The activity of alumina-supported Ce-Mn prepared with different metallic loads and with an equimolar molar composition is shown in Figure 6. As is shown, the mixed oxide samples with 40% metallic load presented more activity than did the samples with 20% and 50%, all prepared by method 2. This behavior is probably related to the higher presence of Mn$^{3+}$ and Mn$^{4+}$ species as shown in the XPS analysis (Figure 4) and its higher specific surface area relative to that of the other equimolar mixed samples with the same metallic load (Table 1). The reactive oxygen species ($O^−$, $OH^−$, $O_2^{2−}$, and $O_2^{−}$) greatly favor the combustion of volatile organic compounds. The presence of these species is evidenced by the BE value of the oxygen atom in these samples (Table 4).

Table 4. Percentage of O, Ce and Mn species of a series of CM0.33 alumina-supported catalysts prepared by methods 1 and 2 and the corresponding simple oxides prepared by method 1

| Catalyst   | O 1s BE(eV) | O 1s BE(eV) | Ce 3d % Ce$^{3+}$ | Ce 3d % Ce$^{4+}$ | Mn 2p BE(eV) | Mn 2p BE(eV) | Mn 2p BE(eV) |
|------------|-------------|-------------|--------------------|--------------------|--------------|--------------|--------------|
| CM0.33-2 (20%) | 100.0       | -           | 16.5               | 83.5               | -            | 26.5         | 31.0         | 42.5         |
| CM0.33-2 (30%) | 531.4       | -           | 17.7               | 82.3               | -            | 19.9         | 27.6         |
| CM0.33-2 (40%) | 531.5       | -           | -                  | 85.7               | -            | 14.1         | 28.3         |
| CM0.33-1 (40%) | 531.5       | -           | -                  | -                  | 14.1         | 57.5         | 28.3         |
| C-1 (40%)    | 531.6       | -           | -                  | -                  | 531.6        | 641.9        | 644.0        |
| M-1 (40%)    | 531.6       | -           | -                  | -                  | -            | -            | -            |

Influence of the method of preparation

The activity of the Ce-Mn alumina-supported samples prepared by different methods and with 40% metallic charge is shown in Figure 5S. As is observed, all the mixed oxides samples present more activity than did the simple oxide supported samples. The activity

![Figure 5. O 2p XPS spectra: deconvoluted peaks with a 40% metallic charge for different methods of preparation, a: M-1, b: CM0.33-1, c: CM0.33-2 and d: C-1](image)

![Figure 6. Ignition curves of mixed oxide alumina-supported catalysts with different amounts of metallic charge prepared by method 2, a: CM0.50-2 (20%), b: CM0.50-2 (40%), c: CM0.50-2 (50%)](image)
Ce$_{\alpha}$Mn$_{1-\alpha}$O$_2$ catalysts supported over γ-Al$_2$O$_3$ prepared by modified redox-coprecipitation methods

The lower activation energy is usually related with the activity of the catalysts and the rate velocity of the reaction, so a better catalyst is expected. The lower the E$_a$ value is (43 kJ/mol), the easier the hexane can be oxidized, and this value was achieved for the sample CM0.33-2 with 40% metallic load. The high catalytic activity can be associated with a better reducibility, high content of Mn$^{4+}$ and Mn$^{3+}$ species as well as the best synergistic interaction between Ce and Mn, achieved through the method of preparation with sodium carbonate.

CONCLUSIONS

The supported Ce-Mn samples showed better activities in n-hexane combustion than did the simple oxides. The sample Ce$_{0.33}$Mn$_{0.67}$O$_2$ prepared by method 2 showed the highest activity, probably due to the enrichment of Mn$^{3+}$ and Mn$^{4+}$ surface species as well as the relatively favorable reducibility related to the corresponding supported single oxides. The alumina-supported Ce-Mn sample prepared by suspension-coprecipitation with the redox reaction with potassium permanganate and Na$_2$CO$_3$ used as a precipitating agent appeared to have the best performance. The sample Ce$_{0.33}$Mn$_{0.67}$O$_2$ precipitated with sodium carbonate exhibited the highest activity for n-hexane combustion, probably due to the better Ce-Mn interaction between the surface species Ce$^{4+}$, Mn$^{3+}$ and Mn$^{4+}$ with the contribution of the metal-support interaction. This sample also showed the highest reducibility and an abundance of superficial oxygen species, which favored the total combustion of n-hexane, revealing the synergistic effect of the Ce-Mn metal interaction.

SUPPLEMENTARY MATERIAL

Figures 1S-5S are freely available at http://quimicanova.sbq.org.br, in PDF format.

ACKNOWLEDGMENTS

The authors want to express their sincerest gratitude to the Research Management Office of National University of Engineering of Lima-Peru (OGI) for the financial support for this work and Dr. Silvia Irusta from Universidad de Zaragoza by the XPS measurements and assisting spectra identification. R. C. wishes to acknowledge FONDECYT (Convenio n°208-2015-FONDECYT) for his Master scholarship.

REFERENCES

1. Ahmad, W.; Noor, T.; Zeeshan, M.; Catal. Commun. 2017, 89, 19.
2. Tang, W.; Wu, X.; Li, S.; Li, W.; Chen, Y.; Catal. Commun. 2014, 56, 134.
3. Spivey, J. J.; Ind. Eng. Chem. Res. 1987, 26, 2165.
4. Jirátková, K.; Kovanía, F.; Balbánová, J.; Kátrorá, P.; Catal. Today 2018, 304, 165.
5. Hu, J.; Li, W. B.; Liu, R. F.; Catal. Today 2018, 314, 147.
6. Hinokuma, S.; Shimanoe, H.; Kawabata, Y.; Kiritoshi, S.; Araki, K.; Machida, M.; Catal. Commun. 2018, 105, 48.
7. Morales, M. R.; Yeste, M. P.; Vidal, H.; Gatica, J. M.; Cadus, L. E.; Fuel 2017, 208, 637.
8. Tang, W.; Li, W.; Li, D.; Liu, G.; Wu, X.; Chen, Y.; Catal. Lett. 2014, 144, 1900.
9. Wu, Y.; Shi, S.; Yuan, S.; Bai, T.; Xing, S.; Appl. Surf. Sci. 2019, 479, 1262.
10. Wang, X.; Yiu, L.; Zhang, Y.; Zhang, T.; Chang, H.; Zhang, Y.; Jiang, L.; Appl. Catal., B 2018, 229, 52.
