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New redox deposition-precipitation method for preparation of supported manganese oxide catalysts

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A new preparation method has been developed to produce homogeneous coatings of manganese compounds on alumina-coated monoliths by redox deposition-precipitation using acetone as solvent. The deposition is produced by reduction of manganese permanganate with ethanol. The Lewis acid sites on the alumina catalyze this reaction. Thus, the precipitation is produced preferentially on the surface of the monolith and not in the bulk of the solution. Monoliths prepared by this method are very active for the complete oxidation of oxygenated volatile organic compounds (VOCs). These monoliths consist of a mixture of complex phases including aluminum, sulfated alumina, potassium sulfate and manganese oxide.

KEY WORDS: metallic monoliths; supported MnO_x catalysts; VOCs abatement; redox deposition-precipitation synthesis.

1. Introduction

Now-a-days, the use of transition metal oxide-based catalysts is an alternative to noble metals for the abatement of volatile organic compounds (VOCs). In particular, manganese oxide is a very active phase for the complete oxidation of oxygenated VOCs [1]. On the other hand, the treatment of high flow emissions requires the use of monolithic devices to minimize pressure drop, but the deposition of manganese over the monoliths is not a simple task. The deposition-precipitation method is an interesting possibility because the monolith can be introduced in the precipitation medium where a slow solubility decrease of the active phase precursor produces their preferential deposition on the monolith surface. The most habitual way to reduce the solubility is the slow increase of the pH produced by addition of an alkali or by the thermal decomposition of urea [2].

We have recently developed a new type of alumina/aluminum monoliths by anodic oxidation of aluminum that is very useful for VOCs abatement [3,4]. Nevertheless, the alumina coating of these monoliths is very sensitive to the impregnation in aqueous medium because it can produce the pore sealing of the alumina coating [5]. This paper presents a new preparation method developed to deposit manganese oxide on alumina from a solution of potassium permanganate in acetone by reduction with ethanol.

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2. Experimental

2.1. Preparation

Alumina/aluminum monoliths have been used as support for the evaluation of this new method. Their preparation has been described elsewhere [3]. Cylindrical monoliths ($L = 30$ mm, $d = 16$ mm, $V = 6$ cm^3) expose about 35 m^2 of alumina developed in a layer of around 15 μm thick presenting pores ranging from 10 to 25 nm over an aluminum foil (100 μm thick).

Catalytic monoliths were prepared using a solution of $KMnO_4$ in acetone of analytical grade, and for the sake of comparison acetone of technical grade and water were used in other preparations. The solution was prepared by dissolving 0.12 g of $KMnO_4$ in 25 ml of high purity acetone (Merck P.A.R). The monolith is introduced in the solution and finally 0.027 g of high purity grade ethanol (Merck P.A.) was added as reducing agent. These initial concentrations correspond exactly to the stoichiometry of equation [4]. The solution with the monolith was kept under agitation for 60 min, and intensely washed with pure acetone. Afterwards, the monoliths in all the preparations were dried at 393 K for 30 min, and finally calcined in air at 723 K for 2 h.

As the reduction of manganese can arrive to several oxidation states, the oxidation of ethanol may result in a considerable number of products, which can make the analysis quite difficult. If we assume that the oxidation of ethanol is only partial and the final product is always CH_3COOH, the number of possible reactions is still

relatively large. For the sake of illustration, in this condition the following reactions may take place depending the final product on the relative proportions of the reactives, the reduction kinetics that alters continuously these relative proportions, the solution pH and the presence of K^+ ions that might change the redox potential through the formation of different manganese potassium mixed oxides.

$$4MnO_4^- + 4CH_3CH_2OH + 4H^+ \rightarrow 4MnO + 5CH_3COOH + 7H_2O \quad (1)$$

$$12MnO_4^- + 13CH_3CH_2OH + 12H^+ \rightarrow 4Mn_3O_4 + 13CH_3COOH + 19H_2O \quad (2)$$

$$2MnO_4^- + 2CH_3CH_2OH + 2H^+ \rightarrow Mn_2O_3 + 2CH_3COOH + 3H_2O \quad (3)$$

$$4MnO_4^- + 3CH_3CH_2OH + 4H^+ \rightarrow 4MnO_2 + 3CH_3COOH + 5H_2O \quad (4)$$

$$2MnO_4^- + 3MnO + 2H^+ \rightarrow 5MnO_2 + H_2O \quad (5)$$

$$MnO_2 + MnO \rightarrow Mn_2O_3 \quad (6)$$

The aqueous solution was prepared dissolving 1.9 g of $KMnO_4$ in 25 ml of water (Panreac P.A.). The wet impregnation was carried out under orbital agitation for 60 min. The monoliths were vigorously drained to eliminate the solution excess, but not washed. Another preparation was carried out by dissolving 1.9 g of $KMnO_4$ in 25 ml of technical grade acetone (Panreac), without reducing agent addition since technical grade acetone contains a certain amount of impurities of reducing character whose amount is determined by the so called permanganate time. The monolith was introduced in the solution, kept under orbital agitation for 60 min and afterwards intensely washed with acetone.

At the same time, two flat straps (2 cm × 3 cm) of the same anodized aluminum used in the monoliths were coated using the redox deposition-precipitation method developed. In order to obtain information of the manganese phase produced, one of the straps was kept in the precipitation medium for 60 min and the other one for 24 h. In the 24-h preparation, a dark precipitate was observed. This precipitate was filtered, washed, dried and calcined as the monoliths. Pure manganese oxides, MnO, Mn_3O_4, Mn_2O_3 and MnO_2, from Aldrich were used as received

2.2. Characterization

Nitrogen adsorption is used to determine the textural properties using a Micromeritics ASAP 2000 with a homemade cell that allows analyzing the complete 6 cm^3 monolith. All the results, isotherm, surface area, and porosity will be referred to a complete monolith.

The kinetics of the reduction of $KMnO_4$ in acetone by ethanol was studied in a diode array spectrometer HP8452A, following the evolution of absorption at 526 nm, using the absorption at 620 nm for background correction [6].

XRD measurements were carried out in a Phillips PW 1729–1820 diffractometer.

SEM-EDX was used to study the morphology and the profiles of distribution of the principal elements in the samples. Experiments were carried out in a JEOL 5400 equipment to which an energy dispersive spectrometer (OXFORD LINK) was coupled.

XPS experiments were performed using Al K_α radiation (15 kV, 20 mA) after degassing the samples in a pretreatment chamber to a vacuum better than 10^{-7} Torr. All the spectra were recorded with a vacuum better than 1×10^{-9} Torr and the energy scale referenced to the spurious C_{1s} signal at 284.6 eV.

The catalytic activity of the prepared monoliths was measured for the complete oxidation of acetone in air reaction. Ignition curves were obtained by heating up to 773 K at 2.5 K/min the monoliths in a 510 mL/min air stream containing 525 ppm of acetone. Acetone conversion was calculated by measuring the acetone disappearance by GC-TCD (HP 5890) and the CO_2 production with an on line IR detector (Sensotrans IR).

3. Results

The amount of manganese oxide loaded on the monolith was calculated by weight difference before and after preparation. The deposited amount was 14.2 mg for the aqueous preparation, 51.8 mg for the preparation with technical grade acetone without addition of reducing agent, and 86.6 mg when the high purity acetone was used with ethanol addition. Both monoliths prepared in acetone presented homogeneous dark brown color. Nevertheless, the monolith prepared in water showed a very heterogeneous color from dark brown to almost white, presenting points where clearly manganese oxide accumulates.

Figure 1 presents the nitrogen adsorption–desorption isotherms of the parent monolith and those of the manganese oxide loaded monoliths prepared in water and in acetone. The isotherm of the parent monolith corresponds to a mesoporous material presenting a surface area of 33 m^2 and a pore volume of 0.16 cm^3 with a narrow pore size distribution with an equivalent pore diameter of 20 nm. After impregnation in water, the isotherm presents dramatic changes: the surface area increases from 33 to 44 m^2, the pore volume decrease from 0.16 to 0.11 cm^3, and the most important, the closing point of the hysteresis loop moves to $P/P_0 = 0.4$

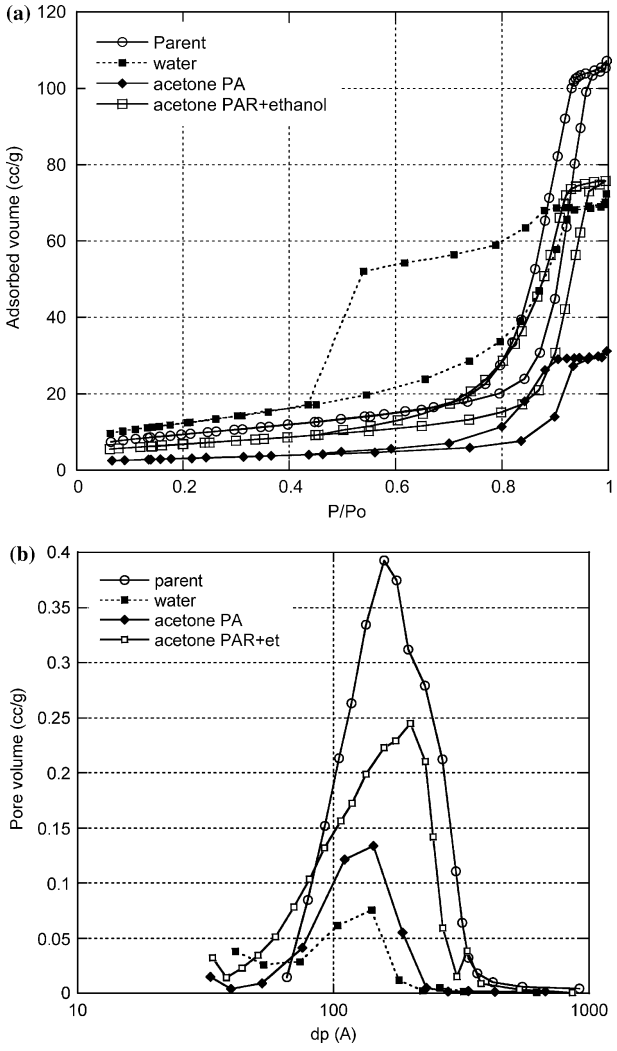

Figure 1. (a) Nitrogen adsorption isotherms of the parent monolith, the monolith impregnated in water and the monolith treated with acetone. (b) Pore volume distribution of the parent monolith, the monolith impregnated in water and the monolith treated with acetone.

indicating an important narrowing of the pore mouth [7]. By contrast, the monoliths treated with acetone do not show changes in the size or shape of the pores. In the case of the monolith prepared with technical acetone, a dramatic diminution of the pore volume is noted, from 0.16 to 0.05 cm^3. In contrast, for the monolith prepared using pure acetone and ethanol, the isotherm is similar to that of the parent monolith with a homogeneous decrease in surface area (33 to 24 m^2) and pore volume (0.16 to 0.12 cm^3) with a similar pore size distribution (figure 1b), that is coherent with a homogeneous deposit of manganese oxide.

In order to understand how the redox deposition-precipitation method works, some kinetic experiments of the reduction of $KMnO_4$ in acetone were carried out. Figure 2 presents the main results of the kinetics. In absence of ethanol, no reduction of the permanganate in acetone is observed when an alumina/aluminum strap is introduced in the cell. If ethanol is added but no

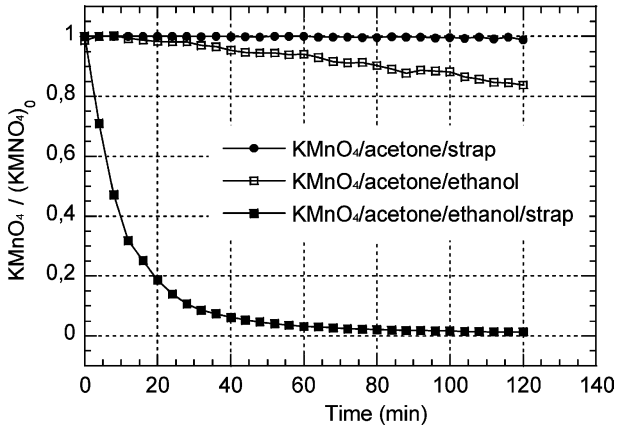

Figure 2. Kinetics of reduction of the potassium permanganate in acetone with the alumina/aluminum strap, with ethanol and with the alumina/aluminum strap + ethanol.

alumina/aluminum strap is introduced, a slow reduction, practically linear with time, of the permanganate is observed and a black solid appears. Finally, in the experiment with the ethanol, when the alumina/aluminum strap is introduced, a catalytic effect in the permanganate reduction is observed, showing that the reaction is almost completed after 60 min.

Figure 3 shows the X-Ray diffraction patterns for straps impregnated by this method for periods of 1 and 24 h, respectively. The pattern corresponding to the precipitated powder produced in the 24-h preparation is also shown. The main crystalline phase present in the powder has been identified as birnessite (b) but several peaks corresponding to other phases are also present in this powder although they could not be identified. For the 1-h strap, no diffraction pattern of manganese oxide is detected. On the other hand, the 24-h strap reflects the presence of a complex mixture of several crystalline compounds. Among these, the birnessite, present in the powder is also identified on the strap. Other phases are also on the strap, as cryptomelane type compounds (c, I and III), and sulfur compounds (II).

In figure 4, the distribution profiles of oxygen, aluminum, sulfur, potassium and manganese along a transversal cut of the alumina/aluminum cermets are shown. The left hand-side of the figure corresponds to the aluminum base matrix, showing only the signal of the aluminum matrix. The central part of the figure corresponds to the alumina layer generated by the anodization process previously described [3], as it can be observed by the presence of aluminum and oxygen. The approximate thickness of this layer, according to figure 4, is 13.5 μm in excellent agreement with the thickness calculated in previous works [3]. In addition, sulfur is present because of the use of H_2SO_4 during the anodization process. Just in this layer, manganese and potassium are deposited, and their profiles show that they penetrate deep in the alumina pores, although they

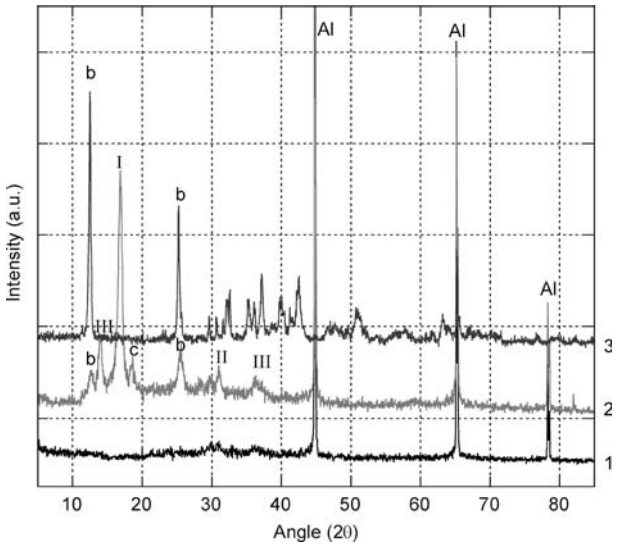

Figure 3. X-ray diffraction patterns of the samples after calcinations at 450 °C for (1) the strap prepared by 1 h, (2) the strap by 24 h, and (3) the powder precipitated in the bulk of the solution. b = birnessite (80-1098), c = cryptomelane ($K_{2-x}Mn_8O_{16}$, 42-1348), Al = aluminum (04-0787), I = $K_{0.5}1Mn_{0.93}O_2$ (70-0192), II = mixture of $K_2S_2O_7$, K_2SO_3, K_2SO_4, $Al_2(SO_4)_3$ and III = K_xMnO_2 (31-1048).

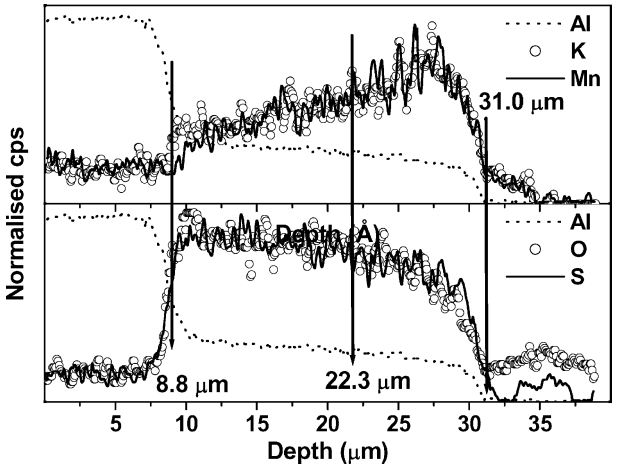

Figure 4. Distribution profiles of oxygen, aluminum, sulfur, potassium and manganese obtained from EDS analysis along a transversal cut of the monolith.

form an uniform external layer of MnO_x of around 7.5 μm. The right hand-side of the figure corresponds to the resin used for preparing the sample.

Figure 5 presents the catalytic tests in the form of ignition curves for the different prepared monoliths. Additionally, one alumina/aluminum monolith loaded with Pt is presented for the sake of comparison. It can be seen that the one prepared with the new method is much more active (T_{50} = 495 K) than the ones prepared in water (T_{50} = 588 K) and in acetone (T_{50} = 548 K). It is even more active than the one loaded with 4 mg of Pt (T_{50} = 513 K). The ignition curve of the sample

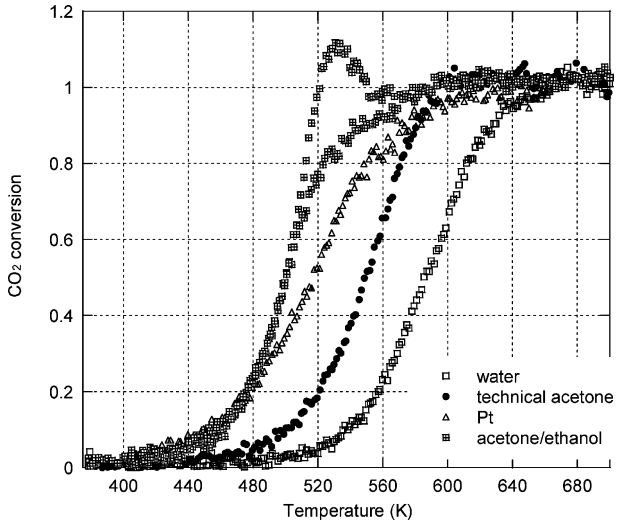

Figure 5. Ignition curve of the complete oxidation of acetone with the monolith loaded with manganese oxide by redox deposition-precipitation and by impregnation in water, and that corresponding to a standard monolith loaded with Pt.

prepared by the new method presents an apparent conversion maximum of 1.15. This kind of behavior has been previously explained by the coupling of adsorption-desorption phenomena of reactants and products at the ignition point [4].

MnOx/Al2O3/Al monoliths prepared with this new method showed a remarkable stability during laboratory tests. In a dedicated isothermal stability test (500 ml/min of air containing 525 ppm of acetone) carried out at 439 K, the conversion decreased from 60% to 56% during the first 20 h, but remained stable at this value for 60 additional hours.

4. Discussion

Monoliths prepared with classical methods using water presented several problems. The first one is that the technique is hardly reproducible because most of the manganese oxide appears forming agglomerates in the corner of the channels at the bottom of the monolith. The amount of these agglomerates depends on the severity of the draining treatment. In addition to that, these agglomerates do not show enough adherence and significant amounts of manganese oxide are lost during the manipulation of the monoliths. Finally, textural changes of the monoliths show a deep modification of the alumina coating suggesting that the manganese oxide do not enter in the porous network of the alumina.

The change in the porosity of the anodic alumina coating is a well-known phenomenon in the aluminum anodization industry that calls it pore sealing [8]. Pore sealing is related to the dissolution-precipitation of the alumina at the pore mouth. This process is accompanied

by the formation and decomposition of aluminum hydroxide that generates some microporosity [8] explaining the surface area increase observed in addition to the narrowing of the pore mouth.

Several attempts to deposit manganese oxide on the monoliths by the classical deposition-precipitation method using alkali solutions to increase the pH, produced unsatisfactory results. The deposition on the monolith was heterogeneous with most of the manganese precipitated in solution as a separate phase and a very important alumina pore sealing that produced a collapse of the texture.

In order to prevent changes in the texture of the alumina, acetone was considered as solvent due to the high solubility of the potassium permanganate in this medium.

The monolith prepared with technical grade acetone shows neither pore sealing nor microporosity. However, the dramatic decrease of the pore volume indicates that the Mn has plugged the pore mouth. This hypothesis is supported by a simple calculation of the volume occupied by the manganese oxide deposited, which is about four times lower than the pore volume decreased. However, the most important conclusion of this experiment was that the manganese was reduced and coated the monolith surface homogeneously, but also appeared as a precipitate.

A literature survey showed that permanganate is used to test the quality of the industrial acetone in the called ''permanganate time'', that is the time required under standard conditions for the disappearance of the permanganate color due to its reduction by the impurities present in the acetone [6]. Therefore, the reduction of the manganese observed when using technical grade acetone could be attributed to the presence of high amounts of impurities. This encourages us to use high purity acetone and ethanol, which is one of the compounds that reduce the permanganate, as redox agent to produce the deposition-precipitation under controlled conditions.

The results obtained were excellent with a homogenous coating of the monoliths that presented a uniform dark brown color, no pore sealing in a very short time with almost no manganese oxide precipitated in the solution. Even though the weight of the oxide deposited on the monolith is higher than in the preparation with technical grade acetone (acetone contaminated with reducing agents, mainly ethanol), the slight pore volume decrease suggests that the Mn has entered the pores, and it is forming a coating not far away from a monolayer. These differences could be explained in terms of the amount of impurities able to be oxidized present in the technical grade acetone. This amount must be higher than the stoichiometric amount of ethanol we add, according to equation [4], to the high purity acetone, producing a very rapid reduction of the manganese that plugs the pore mouth and partially precipitates in the liquid phase.

The kinetic experiments carried in a UV cell help to understand the precipitation mechanism. Figure 2 shows that the alumina/aluminum strap produces a catalytic effect accelerating the permanganate reduction by the ethanol. This catalytic effect can be related to the acidic properties of the anodized alumina. Indeed, Lai and Lee reported that Lewis acids catalyze the reduction of permanganate in acetone by ethanol [9]. In our case, the acidity of the alumina produced by anodization is enhanced by the sulfate arising from the electrolyte (sulfuric acid) that reach 15% by weight of the alumina [3,8].

The manganese oxide phase produced is difficult to identify because it is of a small amount and is forming almost a monolayer. Several attempts using DRIFTS and Raman Spectroscopy did not add significant information. XRD of the flat test specimens prepared in the same conditions than the monoliths (60 min) did not produced valuable information apart from the amorphous character (Figure 3I). The X-Ray diffraction pattern of the strap for 24 h shows the presence of several mixed potassium and manganese oxides deposited over the alumina layer (cryptomelane and K_xMnO_2) but also different oxides to the ones appeared on the powder formed during the long impregnation in the solution (birnessite). The presence of different Mn and K mixed oxides is produced only on the alumina surface. Among them, a crystalline phase corresponding to cryptomelane (c) has been identified. These type of compounds are very interesting due to their molecular sieve structure, which confers them very good properties for adsorption and high activity in the elimination of VOCs [10]. On the other hand, the appearance of some peaks in the strap can be related to the presence of sulfate arising from the anodization in H_2SO_4 ($K_2S_2O_7$, K_2SO_3, K_2SO_4 and even $Al_2(SO_4)_3$. $KMnO_4$ disappears from solution after 120 min according to our UV–vis results (figure 2). Then, the homogeneous coating formed has to evolve in the presence of the acetone solution at least during 24 h, since once the permanganate has been consumed the only possibility for the changes observed in the X-ray diffraction experiments (figure 3) must be due to some of the reactions listed above.

In order to try to characterize the formed deposit and to understand the surface behavior, XPS measurement has been carried out. Manganese oxide systems are not particularly simple for the characterization of manganese oxidation states due to the relative importance of intra- and inter-atomic effects [11]. Two types of intra-atomic many-body, or electron correlation effects are important for the XPS of transition metal (TM) cations; one type is important for the *3s* XPS and the other is important for the *2p* and *3p* XPS [12].

The spectral splitting of the *3s* core-level XPS spectra in TM and their compounds originates from the exchange coupling between the *3s* hole and the *3d*

electrons. The magnitude of the splitting is proportional to $(2S+1)$, where S is the local spin of the *3d* electrons in the ground state. For *3d* metal compounds, the calculated *3s* splitting is more than two times larger than the observed one. It indicates that the observed *3s* splitting is not likely to be due to the spin exchange only. This fact was explained by the intrashell correlation effects between $3s^1 3p^6 3d^n$ and $3s^2 p^4 3d^{n+1}$ configurations [13].

If we follow the Galakhov *et al.* [13] approach and measure the Mn·3*s* spectra of compounds where the formal oxidation state of manganese is known, we can correlate the average spin multiplicity of the manganese cation with the energy differences (δE) between the main peak, for Mn^{2+} a ^7S multiplet, and the satellite, for Mn^{2+} a ^5S multiplet. Figure 6 shows the variation of the formal oxidation state of manganese with the relative energy between the main peak and the satellite peak of the Mn *3s* signal. It is obvious the excellent correlation between these two magnitudes for MnO, Mn_3O_4, Mn_2O_3 and MnO_2 oxides commercially available [14]. In order to test the procedure, the Mn–Al spinel has been prepared according to a previously reported method [15] and measured in the same conditions resulting the manganese in an average oxidation state of +2.06, which is equivalent to a 3% error in the formal oxidation state. For the two alumina/aluminum straps the oxidation states are +2.32 and +3.18 for the straps treated for 1 and 24 h, respectively. These results strongly support the evolution of the manganese deposit in the presence of the acetone solution due to the redox equilibria involved between the deposited manganese species and the organic species present in the acetone solution.

Reproducibility and performance of the new preparation method has been tested showing in all cases a homogeneous coverage of the catalyst, and the most important, showing high activity in the complete elimination of acetone. Because of the promising results of this method, additional studies are currently being carried out in our laboratory on different structured supports. Preliminary results clearly show that this method can be successfully adapted to SiC foams or FeCrAlloy monolith coated with alumina. Because of the previous data, significative evidence for the possibility of tailoring the oxidation state of manganese is obtained and in this way to optimize the catalytic behavior of the prepared catalysts.

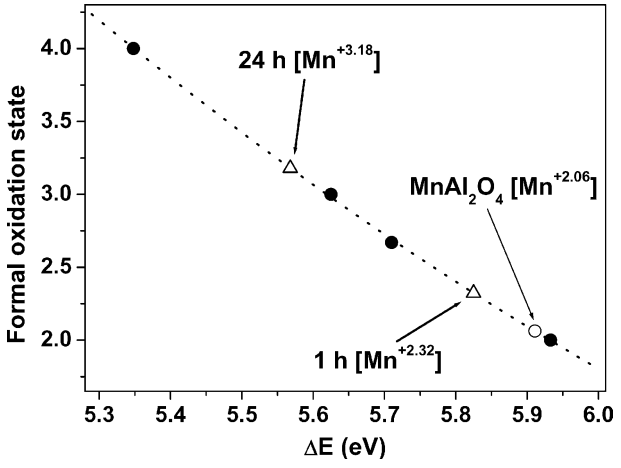

Figure 6. Variation of the formal oxidation state of manganese cation in manganese oxides as a function of the relative energy between the XPS Mn *3s* main peak at its satellite. Full points commercially available oxides.

5. Conclusions

A new preparation method has been developed to produce homogeneous coatings of manganese oxide on alumina by redox deposition-precipitation using acetone as solvent. The deposition is produced by reduction of manganese permanganate by ethanol. This reaction is catalyzed by the acid sites on the alumina surface enhanced by the presence of important amounts of sulfate in the alumina. Thus, the precipitation is produced preferentially on the surface of the monolith and not in the bulk of the solution. The use of acetone as solvent prevents the pore sealing produced by the classical impregnation methods using water.

Some interesting compounds for adsorption and catalytic activity have been identified in the alumina surface, leading to high performance devices. The reproducibility of the method has been confirmed.

Finally, and the most important, the catalytic devices prepared by this method are very active, even more that the standard one we prepare with platinum as active phase, in the complete oxidation of oxygenated VOCs.

Acknowledgments

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