IRON-MANGANESE MIXED OXIDE CATALYSTS FOR ETHANOL COMBUSTION. INFLUENCE OF THE Fe:Mn ATOMIC RATIO AND THE CALCINATION TEMPERATURE

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Abstract— A Fe-Mn mixed oxide catalyst for ethanol combustion was optimized using different Fe:Mn atomic ratios and varying the calcination temperature (500ºC, 650ºC and 800ºC). The results indicated that the increase of the calcination temperature caused a decrease of the catalytic activity due to a strong decrease of the specific surface area. Then, among the catalysts calcined at 500ºC, the most active one was the catalyst with lower amount of iron. The results of X-ray diffraction (XRD) and temperature programmed reduction (TPR) indicated that a small amount of iron in the Fe-Mn mixed catalyst favored the formation of dispersed surface amorphous MnOx species. These species are easily reducible and very active in total oxidation reactions.

Keywords— total oxidation, ethanol, catalyst preparation.

I. INTRODUCTION

In the last decade, ethanol has been considered a promising alternative fuel. It is used in cars as an octane enhancer and an oxygenated additive to gasoline, and even, as a replacement for gasoline (Wang *et al*., 2000; Goldemberg *et al*., 2008). Although exhaust emissions of ethanol are less toxic than those of gasoline, partially oxidized products such as acetaldehyde, CO and acetic ester may cause severe environmental and health problems. For these reasons, it is important to eliminate the pollution of ethanol and their by products, being the catalytic combustion an attractive method. Therefore, it is necessary the development of efficient catalysts, which would directly convert ethanol to CO_2 and H_2O at relatively low temperature.

Several groups have investigated the reactivity of noble metal-based catalysts and transition metal oxide-based catalysts in oxidation reactions. Generally speaking, the noble metal catalysts are more active than other metal oxide catalysts, but they are more expensive and easily poisoned as well. Particularly, manganese oxide-based catalysts have received great attention because they exhibit an interesting behavior in combustion reactions and they are environmentally friendly materials (Wahlberg *et al*., 1999; Gallardo-Amores *et al*., 1999). Their catalytic properties are attributed to a high capacity to store oxygen and to form manganese oxides in different oxidation states, for the reason that manganese is highly efficient in reduction-oxidation cycles. The redox abilities frequently increase if it is combined with other elements (Lin *et al*., 2001). For instance, Mn-Cu mixed oxides show better catalytic behaviour than Mn_2O_3 and CuO pure oxides in the combustion of propane and ethanol (Morales *et al*., 2006).

In a previous work (Morales *et al*., 2007), iron-manganese mixed oxide based catalysts, obtained by coprecipitation showed a higher catalytic activity in ethanol combustion than Mn_2O_3 and Fe_2O_3 pure oxides. Mishra *et al.* (2008) prepared manganese-iron mixed oxide pillared clays with varying the manganese to iron ratio and they observed that the catalyst with higher Mn/Fe ratio was the most active in the acetone decomposition while the catalytic activity in trichloroethylene decomposition increased with the increase in iron content up to certain value (10.14%). These results encouraged us to attempt the optimization of the iron-manganese mixed oxide catalysts prepared by coprecipitation with varying the Fe:Mn atomic ratio and the calcination temperature. The catalytic behavior was evaluated in the ethanol combustion.

II. EXPERIMENTAL SECTION

A. Preparation of the catalysts

Aqueous solutions of $Fe(NO_3).9H_2O$, 0.48M (Riedel-de Haën), $Mn(NO_3).4H_2O$, 0.48M (Fluka), and NH_4OH 1N (used as precipitant agent) were prepared (Wang *et al*., 2005). The nitrate solutions were mixed in adequate proportions for obtaining Fe:Mn atomic ratios equal to 1:1, 3:1, and 1:3. Then, the mixed solution was added drop by drop at the ammonium hydroxide solution kept under agitation and at pH = 11.5 – 12.5. The pH was regulated adding ammonium hydroxide at 28 vol% when it was necessary. Meanwhile, the precipitate was aging in the mother solution for 24 hours. Then, it was separated from the solution and dried slowly in a vacuum oven increasing the temperature from 50ºC to 120ºC at 5ºC/h. The resulting solid was milled and calcined in air at 500ºC, 650ºC or 800ºC for 3 hours. The catalysts were denoted as FexMny-T, where the ratio x:y = 1:1, 3:1, and 1:3 represents the Fe:Mn atomic ratio and T is the calcination temperature in Celsius degrees. Also, Fe_2O_3 and Mn_2O_3 were prepared by the same synthesis method and calcined at 500ºC, for comparison.

B. Characterization of the catalysts

The specific surface areas were measured in a Micromeritics Gemini V equipment by the nitrogen adsorption method (BET) after to degas the samples at 250ºC under N_2 flow using a FlowPrep 060 – Sample

Degas System – from Micromeritics. The crystalline phases were identified by X-ray diffraction (XRD) using a Rigaku diffractometer equipped with a radiation source of V filtered - Cr Kα (λ = 0.22897 nm) operated at 35 kV and 25 mA and the PDF-ICDD files as references. The composition was determined by X-ray fluorescence (XRF) with a Philips PW 1400 apparatus where the calibration standards were prepared with known amounts of Fe_2O_3 and Mn_2O_3. The study of temperature programmed reduction (TPR) was carried out using a U-type quartz tubular reactor and a thermal conductivity detector (TCD) for recording the hydrogen consumption. A 25mg-sample and a reducing gas mixture (5 vol% H_2/N_2) at a flow rate of 30 cm^3/min were used. The temperature was increased at a heating rate of 10ºC/min from room temperature to 700ºC, and kept at that temperature until the hydrogen consumption signal returned to the initial value.

C. Catalytic evaluation

The catalysts were evaluated in the total oxidation of ethanol using a glass fixed bed reactor operated at atmospheric pressure. The powdered catalyst was pelletized to particles of 0.5 – 0.8 mm diameter. The sample (300 mg) was mixed with glass particles of the same size in a weight ratio of catalyst:glass = 1:5. The reactive mixture was $C_2H_5OH:O_2:He$ = 1:20:79 in volume with a total flow rate of 100 cm^3/min. The reaction temperature, measured with a thermocouple placed in the centre of the catalytic bed, was increased from 80ºC until total conversion of ethanol. The reagent and products were analyzed by on-line gas chromatography using a Buck Scientific Mod 910 chromatograph equipped with a Porapak T columm and thermal conductivity detector.

III. RESULTS AND DISCUSSION

In a previous work (Morales *et al.*, 2007), it was observed that an iron-manganese mixed oxide catalyst was more active than the pure oxides, Fe_2O_3 and Mn_2O_3, in ethanol combustion. That catalyst was prepared with a Fe:Mn atomic ratio equal to 1:1 calcining the precipitate at 500ºC. This work attempts to optimize the Fe-Mn mixed oxide catalyst by using different calcination temperatures and Fe:Mn atomic ratios.

The catalyst composition (Fe:Mn atomic ratio) was determined by means of XRF and the results are presented in Table 1. As it can be observed, the experimental values are significantly different from the nominal ones. The Fe:Mn atomic ratio for Fe1Mn1-T series was 1.70±0.04 being 1 the theoretical value; for Fe1Mn3-T series, it was 0.82±0.07 (theoretical value = 0.33), and for Fe3Mn1-T it was 5.71±0.10 (theoretical value = 3). The higher iron proportion detected in all of the catalysts could be due to a difficulty in precipitating the manganese during the preparation stage. In this work, the iron and manganese ions from the nitrate solutions were precipitated as hydroxides using NH_4OH as precipitant agent. The solution pH was kept between 11.5 and 12.5 adding concentrated NH_4OH when it was necessary. However, this practice was not enough to achieve the complete precipitation of the manganese that partially remained in solution.

Compositions closed to the nominal ones were obtained by means of the citrate method (Durán *et al.*, 2009) but this method presents a great difficulty during the period of calcination, where small amounts of sample and low heating rate must be used to avoid an explosion. Therefore, the large-scale catalyst production by the citrate method would be not viable.

Although the nominal Fe:Mn atomic ratios were not achieved in this work, the study was continued since the effect of the composition on the catalytic activity could be evaluated regardless of these values.

Increasing the calcination temperature, structural modifications may be obtained favoring the solid state reaction of the elements which constitute the system. The phase diagram of the Fe-Mn-O system establishes that, under conditions similar to those used in this work for the synthesis of the catalysts, the Fe_2O_3 and Mn_2O_3 phases coexist when the calcination temperature is below 600ºC. At higher temperatures, the formation of solid solutions by substitution has been observed (Kedesdy and Tauber, 1956). However, the results of XRD of our catalysts do not show modifications of the lattice parameters, not even for those catalysts calcined at 800ºC.

Table 1. Results of chemical composition determined by X-ray fluorescence (XRF), specific surface area measured by the BET method and catalytic activity in ethanol combustion.

Catalyst	Fe:Mn atomic ratio	S_{BET} (m^2/g)	X_{200} (%)	Catalytic activity		
				T_{10} (ºC)	T_{50} (ºC)	T_{80} (ºC)
Fe1Mn1-500	1.66	67.0	81	116	172	199
Fe1Mn1-650	1.74	8.3	47	140	202	227
Fe1Mn1-800	1.67	3.9	36	147	219	250
Fe1Mn3-500	0.81	60.0	86	105	167	195
Fe1Mn3-650	0.89	11.4	52	144	198	221
Fe1Mn3-800	0.76	4.8	27	173	221	244
Fe3Mn1-500	5.61	74.0	78	110	178	201
Fe3Mn1-650	5.73	16.2	63	122	188	213
Fe3Mn1-800	5.81	4.1	45	132	208	238
Fe_2O_3		15.9	12	196	258	282
Mn_2O_3		27.4	48	151	202	224

T_{10}, T_{50}, and T_{80}: reaction temperatures corresponding to 10%, 50%, and 80% conversion of ethanol, respectively.
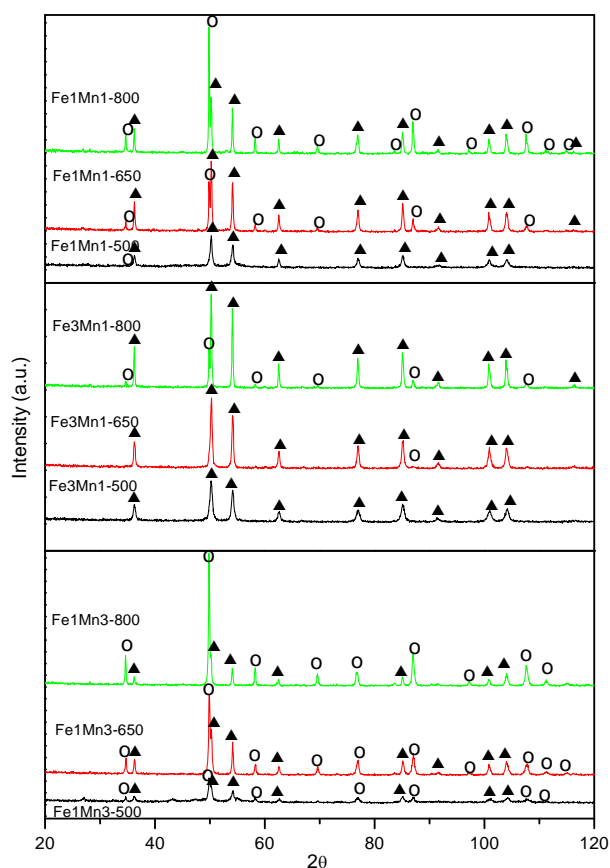
X_{200}: Ethanol conversion at 200ºC.

Figure 1. X-ray diffractograms. (o) Mn_2O_3; (▲)Fe_2O_3.

In fact, only the diffraction lines of Fe_2O_3 (PDF 24-72) and Mn_2O_3 (PDF 24-508) are observed in the X-ray diffractograms (Fig. 1). The relative intensities of each phase are different, depending mainly on the Fe:Mn atomic ratio and, in lesser extent, on the calcination temperature. The Fe_2O_3 phase is detected in all catalysts while Mn_2O_3 is not detected in Fe1Mn1-500, Fe3Mn1-500, and Fe3Mn1-650 catalysts. Then, in these catalysts, manganese could be forming amorphous MnOx species dispersed on the surface, or microcrystalline Mn_2O_3 (crystals smaller than 40Å). The results of temperature programmed reduction (Fig. 2) are in agreement with this assumption. The reduction curve of Fe1Mn1-500 catalyst shows a very broad and weak signal beginning at approximately 200ºC which may be assigned to the reduction of amorphous MnOx species. The curve of Fe3Mn1-500 catalyst also presents a deviation from the baseline beginning at 200ºC and, although this is not defined as a reduction signal, it couldbe considered as an insight into the existence of amorphous MnOx species in a smaller amount than in the Fe1Mn1-500 catalyst. The increase of calcination temperature at 650ºC for Fe3Mn1-T catalysts could be favoring the crystalline order of MnOx species towards the formation of microcrystalline Mn_2O_3, which reduction occurs at higher temperature than 400ºC. A subsequent increase of the calcination temperature at 800ºC

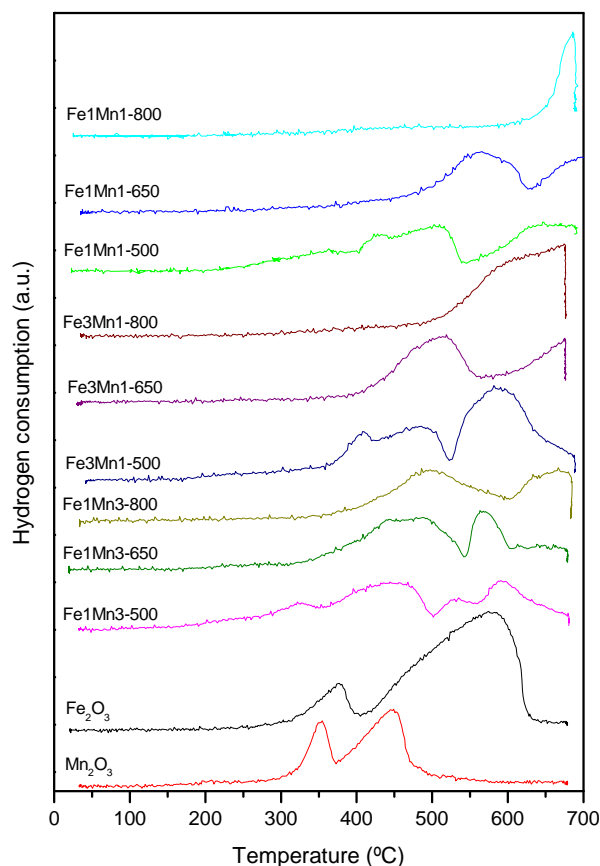induces the growth of Mn_2O_3 crystals which are detected by XRD.

Figure 2. Curves of temperature programmed reduction.

The Fe_2O_3 phase detected by XRD in all catalysts is also affected by the calcination temperature. Applying the Scherrer's equation, it was corroborated that the increase of calcination temperature increases the size of Fe_2O_3 crystals. For instance, in the case of Fe3Mn1-T catalysts, crystal sizes are 259, 432, and 642 Å when the catalysts are calcined at 500, 650, and 800ºC, respectively.

The increase of the crystal size caused by the increase of calcination temperature is in agreement with the decrease of the specific surface area. As it is observed in Table 1, the increase of calcination temperature from 500ºC to 650ºC causes a decrease of around 80% of the specific surface area. The subsequent increase of calcination temperature up to 800ºC causes a decrease in the area resulting 6 – 8% of the value obtained at 500ºC. These results show clearly that the increase of calcinations temperature provokes sintering of particles and breakdown of porous structure.

The specific surface area is a very important characteristic of the solid to be used as catalyst. Therefore, from the catalytic viewpoint, the effect of the calcination temperature on the specific surface area could be more relevant than the effect on the structure of the active phase. Effectively, a decrease of the catalytic activity with an increase of the calcination temperature is ob-

served when comparing T_{10}, T_{50}, T_{80} (reaction temperatures corresponding to 10%, 50%, and 80% conversion,

respectively), or conversion at 200ºC (Table 1).

Table 2. T_{50} and specific surface areas for different catalyst series.

Catalyst	T_{50} (ºC)	S_{BET} (m²/g)	Reference
Fe1Mn3-500	167	60	This work
MnFe-X (Mn:Fe = 1:1; X: aging time)	172	~34	Morales et al., 2007
FeMn 1:3 500	165	60	Durán et al., 2009
FeMn 1:1 500	150	85	Durán et al., 2009
MnNi-X (Mn:Ni = 1:1; X: aging time)	194	~34	Morales et al., 2007
MnCu-X (Mn:Cu = 1:1; X: aging time)	>179	19 - 22	Morales et al., 2006
Mn2Cu8-500	167	43	Morales et al., 2008
Mn2 (cryptomelane)	163	71	Santos et al., 2010
Mn4 (cryptomelane; α-Mn_2O_3)	185	45	Santos et al., 2010
Mn5 (cryptomelane; Mn_3O_4)	147	84	Santos et al., 2010
Mn6 (cryptomelane; α-Mn_2O_3; Mn_5O_8)	163	59	Santos et al., 2010
Mn7 (α-Mn_2O_3; β-MnO_2)	185	46	Santos et al., 2010
$LaCo_{1-y}Fe_yO_3$ (y = 0, 0.1, 0.3, 0.5)	>196	10 - 14	Merino et al., 2006
$La_{1-x}Ca_xFeO_3$ (x = 0, 0.2, 0.4)	>273	13 - 19	Barbero et al., 2006
$La_{1-x}Ca_xMnO_3$ (x = 0, 0.1, 0.2, 0.3)	>173	22 - 26	Stege et al., 2011
$La_{0.6}Sr_{0.4}MnO_3$	174	n.r.	Wang et al., 2000
6%Ag/$La_{0.6}Sr_{0.4}MnO_3$	144	n.r.	Wang et al., 2000

n.r.: not reported

These results lead to the partial conclusion that the increase of the calcination temperature is not convenient to optimize the mixed FeMn catalyst since the decrease of the specific surface area has more influence on the catalytic activity than the formation of a solid solution or other structural change of the active phase. In consequence, in order to reveal which is the most convenient Fe:Mn atomic ratio, only the catalysts calcined to the lowest temperature (500ºC) are considered.

To compare the catalytic activity, the values of T_{50}, T_{80} or conversion at 200ºC (presented in Table 1) are taken into account. Although the differences are small, there is a clear tendency. The activity of the catalysts calcined a 500ºC decreases in the following order: Fe1Mn3-500 > Fe1Mn1-500 > Fe3Mn1-500. Furthermore, it is worth to note that the specific surface area decreases with the decrease of the iron content (Fe3Mn1-500 > Fe1Mn1-500 > Fe1Mn3-500). Therefore, considering the intrinsic activity (conversion per square meter of surface area), it is deduced that the mixed iron-manganese oxide catalyst with low proportion of iron (Fe1Mn3-500) is the most active one for ethanol combustion.

Similarly to Fe1Mn1-500 and Fe3Mn1-500 catalysts, the reduction of Fe1Mn3-500 catalyst begins around 200ºC and a reduction peak with the maximum at approximately 325ºC (Fig. 2) is detected. This signal could be assigned to the reduction of amorphous MnOx species dispersed on the surface. Then, considering that the area under the reduction curve between 200ºC and 350ºC is proportional to the amount of dispersed MnOx species, an increase of the catalytic activity with a higher amount of these species is clearly observed.

The dispersed surface amorphous MnOx species has been recognized as highly reactive in oxidation reactions because they are easily reducible. The close relationship between the results of catalytic activity and the amount of these species detected in the catalysts leads to propose that the ethanol oxidation on mixed Fe-Mn cat-

alysts takes place through a redox mechanism generally known as Mars – van Krevelen. This mechanism has been also suggested on other mixed Mn-Ni (Morales et al., 2007) and type-perovskite $La_{1-x}Ca_xFeO_3$ oxide catalysts (Barbero et al., 2006).

Consequently, the best catalytic activity of Fe-Mn mixed catalysts in comparison to pure Mn_2O_3 can be attributed to the formation of amorphous MnOx species favored by the presence of a small amount of iron.

In order to evaluate the level of optimization of the Fe-Mn mixed oxide catalyst achieved in this work, a comparison of the catalytic performance of Fe1Mn3-500 with other catalysts is carried out. In Table 2, T_{50} and specific surface areas for several catalysts are presented. First of all, it is interesting to compare Fe1Mn3-500 catalyst with other Fe-Mn catalysts prepared by different methods. As it is observed, T_{50} for Fe1Mn3-500 is lower than for FeMn-X (atomic ratio Fe:Mn = 1:1), which was prepared by coprecipitation with $NaCO_3$ at different aging time of the precipitated. In relation to Fe-Mn catalysts prepared by the citrate method (Durán et al., 2009), Fe1Mn3-500 is quite similar to FeMn 1:3 but less active than FeMn 1:1 catalyst. Probably, a different structure -besides of a higher specific surface area generated by the citrate method- is the cause of higher catalytic activity. The advantage of Fe1Mn3-500 catalyst is a simpler preparation method than the citrate method. Regarding to other catalyst families such as MnNi 1:1 and MnCu 1:1, prepared by coprecipitation with $NaCO_3$, Fe1Mn3-500 is more active. Only the optimized Mn-Cu catalyst, Mn2Cu8-500 (Morales et al., 2008), presents the same T_{50} than Fe1Mn3-500.

Comparing with other authors' results is not easy since different reaction conditions were employed. However, we included in Table 2 the results obtained with a family of manganese oxides with different structures (Santos et al., 2010), which are considered as highly active in ethanol combustion. As it can be observed, the activity of Fe1Mn3-500 is similar to Mn2

(cryptomelane) and Mn6 (cryptomelane; α-Mn$_2$O$_3$; Mn$_5$O$_8$). Only Mn5 (cryptomelane; Mn$_3$O$_4$) is more active than Fe1Mn3-500.

With regard to several perovskite-type catalyst series (LaCo$_{1-y}$Fe$_y$O$_3$, La$_{1-x}$Ca$_x$FeO$_3$, La$_{1-x}$Ca$_x$MnO$_3$) evaluated under the same reaction conditions, Fe1Mn3-500 catalyst is considerably more active. Just an addition of Ag to La$_{0.6}$Sr$_{0.4}$MnO$_3$ (Wang *et al*., 2000) increases the catalytic activity giving a T$_{50}$ lower than Fe1Mn3-500 catalyst.

IV. CONCLUSIONS

The optimization of the mixed Fe-Mn oxide catalyst for ethanol combustion was achieved in this work. The results related to the catalytic activity showed that it is not convenient to increase the calcination temperature above 500ºC because the specific surface area strongly decreases. On the other hand, a small amount of iron is enough to favor the formation of dispersed surface amorphous MnOx species which are easily reducible and very active in oxidation reactions.

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