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Catalytic combustion of ethanol on pure and alumina supported K-Mn oxides: An IR and flow reactor study

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Abstract

Mn-based catalysts prepared by oxidation of Mn(II) by KMnO_4 , pure and supported on alumina, calcined at 350 and 500 °C have been characterized and tested in the total oxidation of ethanol. IR experiments allowed us to have an indication on some aspects of the reaction mechanisms. The unsupported catalysts calcined at 350 °C, mostly constituted by a cryptomelane phase were the most active, allowing the total conversion of ethanol at 180 °C, with excellent stability for at least 80 h. The reaction is initiated by the fast conversion of ethanol to acetate species via acetaldehyde. Later, the conversion of acetates to CO_2 appears to be a slow step. On alumina-supported catalysts, which are (in spite of the much higher surface area) active only above 240 °C, part of acetate species are adsorbed on the support and act as inactive spectators.

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1. Introduction

The manganese oxides [1,2], including bulk MnO_2 [3,4], Mn_2O_3 [5] and Mn_3O_4 [6], as well as Mn oxides supported on carriers such as silica, alumina [7,8], titania [9,10] and zirconia [11] are very interesting materials in the field of environmental catalysis. In particular, MnO_x showed an interesting behaviour in the catalytic combustion of hydrocarbons and oxygenated volatile organic compounds (VOC's) [11,12]. They are themselves environmentally friendly materials [11] and find application in the industrial waste gas treatment processes such as those resulting from acrylonitrile synthesis [13]. However, due to the very high activity of these materials as oxidation catalysts, it has been found that, working at low contact time, they can also behave as quite efficient partial oxidation catalysts, such as for carbonyl compounds formation from alcohols on Mn_3O_4 [14]. In the total catalytic combustion processes for VOC's, partial oxidation reactions must be

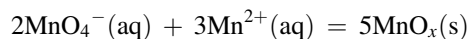
avoided. According to more strict limits for the emissions of some partially oxidized compounds, the presence of even small amounts of species like aldehydes, can make the mixture resulting from catalytic combustion processes even more pollutant than the waste to be purified [15].

In the present paper, we report our studies of the total oxidation of ethanol over Mn-based catalysts prepared by oxidation of Mn(II) by KMnO_4 . The preparation of the catalyst is relevant because the open structure of the solid and the presence of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple allow K-Mn oxides to have interesting physicochemical properties such as a high capacity of adsorption and a high electrical conductivity, which different authors have shown is related to the catalytic performance [16,17].

2. Experimental

2.1. Preparation of the catalysts

Four kinds of solids were prepared by reaction of $\text{Mn}(\text{NO}_3)_2$ solution with KMnO_4 .



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Then 50 mL of $\text{Mn}(\text{NO}_3)_2$ 0.05 M (per analysis) was added drop wise to 50 mL of KMnO_4 0.5 M (Anhydrous 99%), and the suspension was stirred at 30 °C for 1 h. The product was filtered, washed with distilled water and dried at 120 °C for 24 h. Finally, the solid was calcined in air at 350 and 500 °C for 2 h. The oxides are designated MK1-350 and MK1-500 hereinafter.

Two other solids were prepared by drop wise addition of KMnO_4 to $\text{Mn}(\text{NO}_3)_2$. The solids were dried at 120 °C and calcined at 350 and 500 °C. These are designated as MK2-350 and MK2-500. The supported K-Mn oxides/ Al_2O_3 were synthesized by the conventional wet impregnation method using an aqueous solution of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 . Four samples were prepared in a similar manner as described above (MK1A-350, MK1A-500, MK2A-350 and MK2A-500).

The Mn concentration, like MnO_2 , in the MK1A and MK2A catalysts was analysed by titration with oxalic acid.

2.2. Characterization

The catalytic materials were characterized by powder X-ray diffraction method using a Phillips Diffractometer. The diffraction patterns were recorded using $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation at scanning speed of 2° min^{-1} . The diffraction patterns were taken at room temperature in the range $5^\circ < 2\theta < 70^\circ$. Surface area values of the synthesized samples were obtained by BET method using Micromeritics ASAP 2000.

2.3. Catalytic study

A catalytic test was carried out at atmospheric pressure in a continuous flow tubular glass reactor. The feed gas contained 900 ppm of ethanol in air, with an excess of O_2 . 20 mL min^{-1} of ethanol-air mixture was fed over 200 mg of the sample, loaded in the form of fine powder, which gives a space velocity of 6000 h^{-1} . Catalytic tests were performed at temperature range of 100–300 °C, which was measured using a thermocouple projecting into the centre of the bed. The ethanol conversion was analysed by gas chromatography using a Thermofinnigan Trace CG.

2.4. IR study

Self-supporting pressed disks of the pure catalyst powders were activated “in situ” in the IR cell by outgassing at 450 °C before the adsorption experiments. A conventional gas manipulation/outgassing ramp was connected to an IR cell, which allowed heating. The adsorption/desorption process has been studied by transmission FT-IR. The sample was saturated with ethanol (up to 20 Torr) in the cell, until the intensity of the adsorbed species has raised a maximum. IR spectra were later collected evacuating at increasing temperatures.

3. Results and discussion

3.1. Characterization of the catalysts

The XRD spectra of the unsupported catalysts can be seen in Fig. 1. In both MK1-350 and MK2-350 catalysts the peaks at

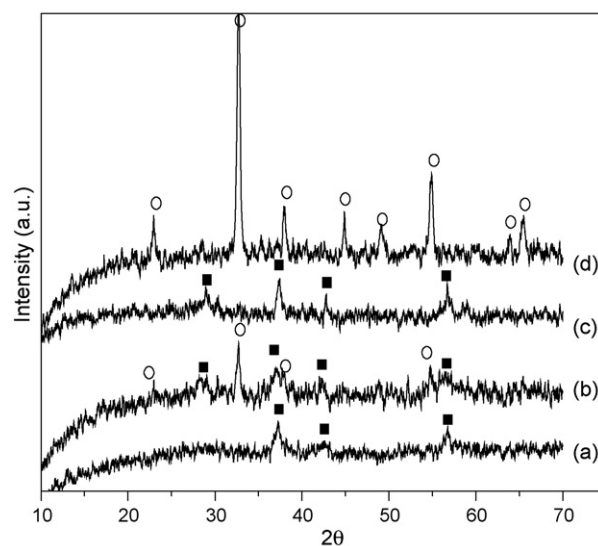


Fig. 1. X-ray powder diffraction patterns of MK samples: (a) MK1-350, (b) MK1-500, (c) MK2-350 and (d) MK2-500 (references (○) Mn_2O_3 ; (■) cryptomelane).

37.2° (2 1 1), 42.7° (3 0 1) and 56.4° (6 0 0) are detected and only in the MK2-350 sample, one signal at 28.6° is observed. At 350 °C the phase formed is cryptomelane, whose chemical molecular formula can be written as $\text{K}_x\text{Mn}_{8-x}^{4+}\text{Mn}_x^{3+}\text{O}_{16}$ ($0.2 \leq x \leq 1$). When the calcination temperature was 500 °C in both MK1 and MK2 catalysts all peaks observed belong to α - Mn_2O_3 (bixbyite, $2\theta = 32.9^\circ$, 23° and 55°).

Fig. 2 shows the X-ray diffraction pattern of MK1A and MK2A catalysts calcined at different temperatures and Al_2O_3 . In the first place, we can see the characteristic peaks of γ - Al_2O_3 ($2\theta = 37^\circ$, 45° and 67°). When the temperature of calcination is 350 °C in both MK1A and MK2A samples three peaks can be observed ($2\theta = 28.6^\circ$, 42.7° and 56.4°) together with the Al_2O_3 peaks. These results showed that in both samples the cryptomelane phase was formed. When the solids were calcined at 500 °C, the situation is different. In MK1A-500,

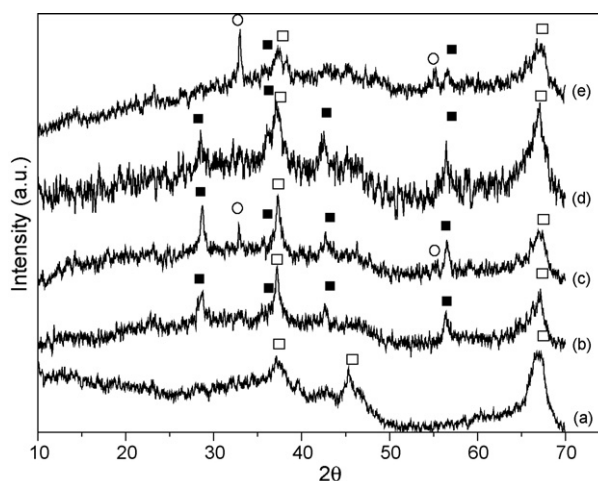


Fig. 2. X-ray powder diffraction patterns of MKA samples: (a) Al_2O_3 , (b) MK1A-350, (c) MK1A-500, (d) MK2A-350 and (e) MK2A-500 (references (□) Al_2O_3 ; (○) Mn_2O_3 ; (■) cryptomelane).

Table 1
Characterization of the MK catalysts

| Sample | Calc. temperature (°C) | Pore volume (cm ³ g ⁻¹) | S _{BET} (m ² g ⁻¹) |
|---------|------------------------|--|--|
| MK1-350 | 350 | 0.34 | 82.3 |
| MK1-500 | 500 | 0.19 | 39.0 |
| MK2-350 | 350 | 0.29 | 68.3 |
| MK2-500 | 500 | 0.16 | 30.8 |

three peaks were observed at 28.7°, 42.7° and 56.6° but one small diffraction peak is detected at 32.9°, which is assigned to Mn₂O₃. In the case of MK2A-500, the main crystalline phase is α-Mn₂O₃. The presence of cryptomelane phase in MK1A-500 sample is associated with the method of preparation. In this sense, Kapteijn et al. [8] have shown by IR spectroscopy that the interaction Mn–Al is strong and survives the calcination. Therefore, this type of the bond stabilizes the cryptomelane phase.

The results of the surface area and volume pore are summarized in Table 1. As it can be seen, the MK1-350 surface area is larger than that of MK2-350 sample. As regards the total pore volume, the same behaviour is observed. According to Post et al. [18], this result may be due to the effect in the parameters of unit cell originated by the Mn³⁺ distortions which is of the order of 0.04 nm.

The properties of the cryptomelanes like acidity and pore size can be modified for example by altering the method of preparation, temperature, etc. In this sense, Ding et al. [19] have demonstrated that the preparation has great influence over the morphology, structural properties and catalytic activity. In this work, MK1-350 sample has a higher surface area and total pore volume than that of MK2-350 solid. According to Shen et al. [20] and Luo et al. [21] the cryptomelane preparation is favoured when the pH solution is acid. The Mn(NO₃)₂ hydrolysis, which produces an acid solution, could be consequence of the structural properties of MK.

The Mn concentration in the supported catalysts, like MnO₂, was 7.5 ± 1.5%. Table 2 shows the surface area of MKA catalysts and Al₂O₃. The surface area is a function of the calcination temperature but it is independent of the preparation methods, but as we have said above the presence of cryptomelane phase is consequence of the Mn–Al interaction.

3.2. Catalytic data

The catalytic tests were tested in the reaction of oxidation of ethanol. In all the experiments, carbon dioxide, water and acetaldehyde were the reaction products.

The ignition curves of ethanol on MK catalysts are shown in Fig. 3. Both MK1-350 and MK2-350 samples have a catalytic performance that is higher than the MK catalysts calcined at 500 °C (MK1-500 and MK2-500). The MK samples calcined at 350 °C, MK1-350 and MK2-350, show a T₅₀ temperature (temperature at which the conversion is 50%) of 155 and 165 °C, respectively. This result is according to the surface areas values of the samples, 82 m² g⁻¹ for the MK1-350 and

Table 2
Characterization of the MKA catalysts and the support

| Sample | S _{BET} (m ² g ⁻¹) |
|--------------------------------|--|
| Al ₂ O ₃ | 200 |
| MK1A-350 | 175.6 |
| MK1A-500 | 164.0 |
| MK2A-350 | 176.0 |
| MK2A-500 | 164.7 |

68 m² g⁻¹ for the MK2-350. Acetaldehyde was found at conversion levels below 40%, in the temperature range of 100–150 °C.

Fig. 4 shows the catalytic performance of the MKA samples calcined at 350 and 500 °C and Al₂O₃. As in the case of the unsupported catalysts calcined at 350 °C, the supported K-Mn oxide calcined at 350 °C has a lower T₅₀ than the supported catalysts calcined at 500 °C although the difference between T₅₀ in the case of the supported catalysts is lower than the unsupported K-Mn oxides. According to Post et al. [18], Chen et al. [22] and previous works [1,4] the best catalytic

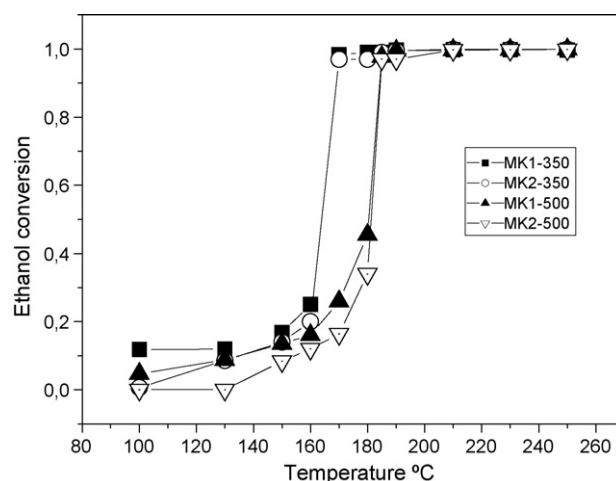


Fig. 3. The ignition curves of ethanol on the MK catalysts.

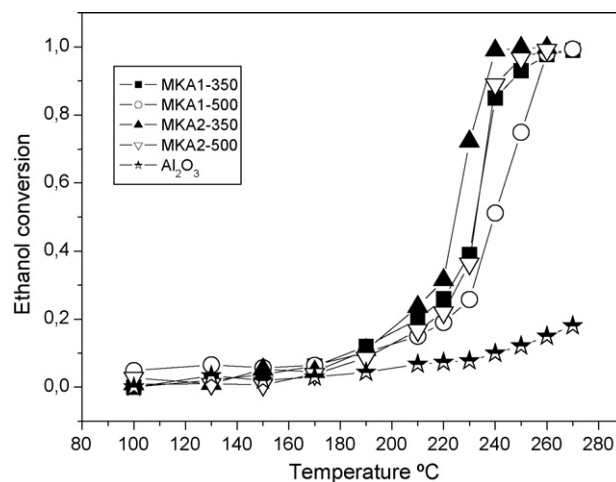


Fig. 4. The ignition curves of ethanol on the MKA catalysts.

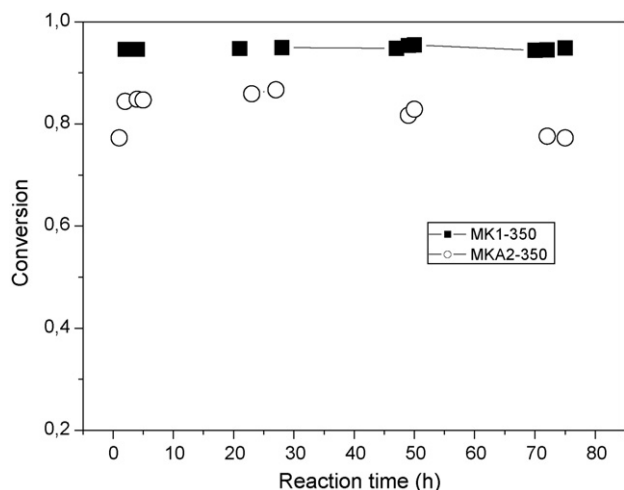


Fig. 5. Stability test: ethanol conversion as a function of reaction time.

performance could be due to the presence of Mn^{3+}/Mn^{4+} couple, oxygen vacancies and OH groups.

Fig. 5 shows the stability test of the MK catalysts. Titled MK1-350 catalyst presents a very good stability which is constant during the study. In the case of MK2A-350, at initial moment (5 h) the activity increased, but after 30 h the catalytic activity decreased and it reached a value that is similar to the initial ethanol conversion. This behaviour can be consequence of different effects. In the first place, different authors showed that ketones and acetates are adsorbed initially (intermediates of reaction) and after that they can react. According to Parida and Kanungo [23] and Lahousse et al. [24] the formation of water during the oxidation reaction is a problem, because H_2O can interact with the active sites, where VOCs are adsorbed, and the catalytic performance decreases with reaction time.

3.3. IR study of ethanol adsorption and oxidation

In Fig. 6, the spectra of ethanol adsorbed over the catalyst MK1-350 are reported. Adsorption at room temperature gives rise to the formation of strong bands at 1097 and 1050 cm^{-1} , and a weaker one at 881 cm^{-1} (see Table 3). The bands at 1050

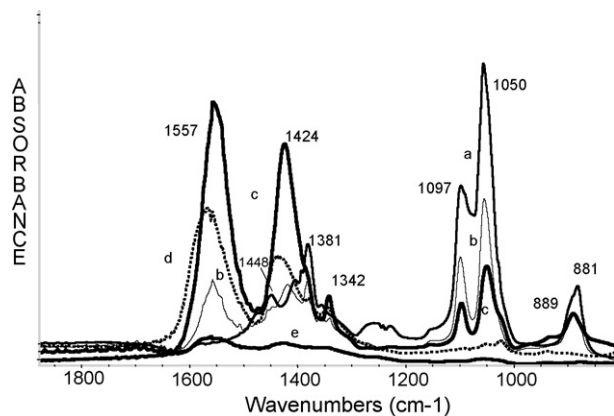


Fig. 6. FT-IR subtraction spectra of the adsorbed species arising from ethanol adsorption on MK1-350 sample (a) adsorbed at r.t.; outgassed at (b) r.t., (c) 100 °C, (d) 150 °C and (e) 200 °C.

Table 3

Assignment of the typical IR bands of surface species

| Acetate groups | Adsorbed acetaldehyde | Ethoxy-groups | |
|------------------|-----------------------|---------------------------|-----------|
| | | | |
| $\nu_{as\ COO}$ | ν_{CO} | | |
| 1600–1550 | 1700–1650 | | |
| | | δ_{wagCH_2} | 1460–1470 |
| | | δ_{asCH_3} | 1450–1440 |
| $\nu_{sym\ COO}$ | | δ_{symCH_3} | 1385–1375 |
| 1450–1400 | | | |
| δ_{CH_3} | | ρ_{CH_2} | 1170–1160 |
| 1360–1340 | | ρ_{CH_3}/ν_{CO} | 1150–1080 |
| | | $\nu_{CO}/\nu_{CC_{as}}$ | 1080–1040 |
| | | $\nu_{CO}/\nu_{CC_{sym}}$ | 900–870 |

and 880 cm^{-1} can be attributed to the asymmetric and symmetric stretching modes of the C–C–O system, while the band at 1097 cm^{-1} is essentially a CH_3 rocking mode also having a CO stretching character [25]. A multiple absorption with maxima at 1381 ($\delta_{sym\ CH_3}$) and at 1448 cm^{-1} ($\delta_{as\ CH_3}$) is due to the deformation modes of the CH bonds. Upon outgassing at r.t. the band at 881 cm^{-1} shows the most stable component at 889 cm^{-1} . The absence of evident bands in the region 1350–1250 cm^{-1} , where the COH deformation mode of ethanol should be observed, provides evidence of the predominance of dissociated ethanol adsorbed in the form of ethoxide groups. After outgassing at room temperature these bands decrease significantly in intensity but a couple of new well evident bands appear at 1558 and 1418 cm^{-1} . After outgassing at 100 °C, these bands are very intense at 1557 and 1424 cm^{-1} , with an additional sharp component at 1342 cm^{-1} . These bands can be assigned confidently to acetate species (asymmetric and symmetric COO stretching, and CH_3 deformation). Under these conditions, the bands of ethoxy groups are still observed to be weak. After outgassing at 150 °C the bands of acetate species have already decreased in intensity and shifted upwards to 1569 and 1433 cm^{-1} , while those of ethoxy groups fully disappeared. After outgassing at 200 °C the bands of acetates also fully disappeared. The data observed here can be compared with those discussed above, concerning the catalytic activity measured on the same catalyst in ethanol combustion. We showed that the conversion of ethanol over this catalyst is relatively low (<20%) at 150 °C and becomes total at 160 °C. At this temperature, the surface becomes to be fully clean while below 150 °C acetates are still very evident.

The IR results on the catalyst MK1-500 are similar (Fig. 7), although the intensity of the bands due to the adsorbed species is definitely lower, likely due to the lower catalyst surface area. The position of the main bands having a CO stretching character is a slightly higher for MK1-500 than for MK1-350. The bands due to ethoxy-groups have already disappeared after outgassing at 150 °C, when the bands of acetate groups show

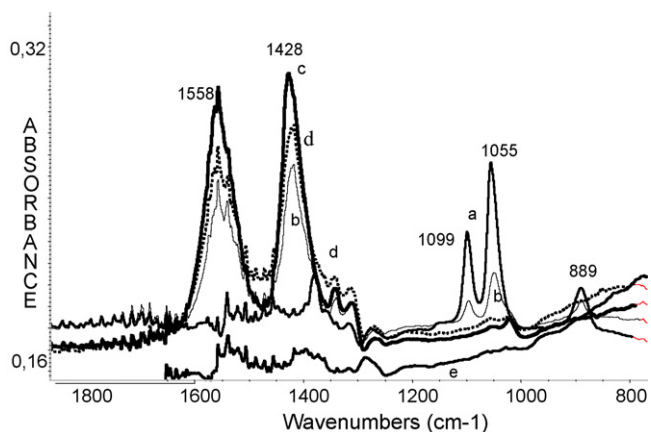


Fig. 7. FT-IR subtraction spectra of the adsorbed species arising from ethanol adsorption on MK1-500 sample (a) adsorbed at r.t.; outgassed at (b) r.t., (c) 100 °C, (d) 150 °C and (e) 200 °C.

their maximum. Later, the bands of acetate decreased until fully disappeared after outgassing at 250 °C. The spectra show a higher stability of acetates in the case of MK1-500 in regards to MK1-350, which should be associated to the lower catalytic activity, with a shift of the light off temperature upwards of 20 °C.

The spectra relative of ethanol adsorption and conversion on MK2-350 are reported in Fig. 8. The picture is similar again. In this case we can also observe, after outgassing at 100 °C, a weak C=O stretching band at 1687 cm⁻¹, certainly due to adsorbed acetaldehyde. At 200 °C, some absorption is still evident in the region 1600–1300 cm⁻¹ due to residual acetates but also likely to carbonates.

In Fig. 9 the analogous spectra recorded for sample MK2-500 are shown. In addition, in this case, as for MK1-500, the bands due to acetates are still observed after outgassing at 200 °C, in agreement with the lower catalytic activity of the sample.

In Figs. 10 and 11, the spectra relative to the adsorption and evolution of ethanol on the alumina-supported samples MK1Al and MK2Al are reported. Although the overall picture has similarities, several important differences are observed here.

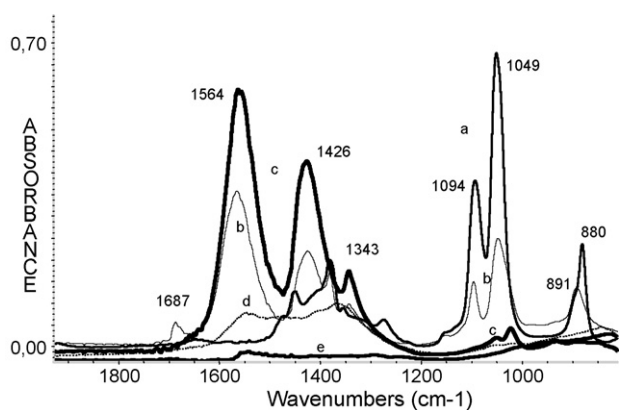


Fig. 8. FT-IR subtraction spectra of the adsorbed species arising from ethanol adsorption on MK2-350 sample (a) adsorbed at r.t.; outgassed at (b) r.t., (c) 100 °C, (d) 150 °C and (e) 200 °C.

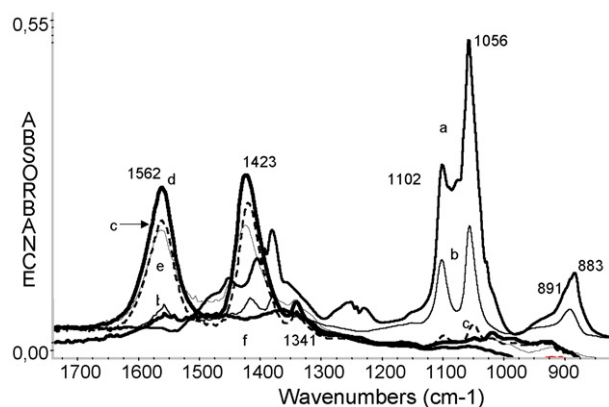


Fig. 9. FT-IR subtraction spectra of the adsorbed species arising from ethanol adsorption on MK2-500 sample (a) adsorbed at r.t.; outgassed at (b) r.t., (c) 100 °C, (d) 150 °C, (e) 200 °C and (f) 250 °C.

The position of the absorption modes of ethoxy species are definitely shifted, to near 1166, 1125 and 1075 cm⁻¹, in regards to near 1100 and 1050 cm⁻¹ for the unsupported catalysts. In addition, the position of the bands of acetates is definitely

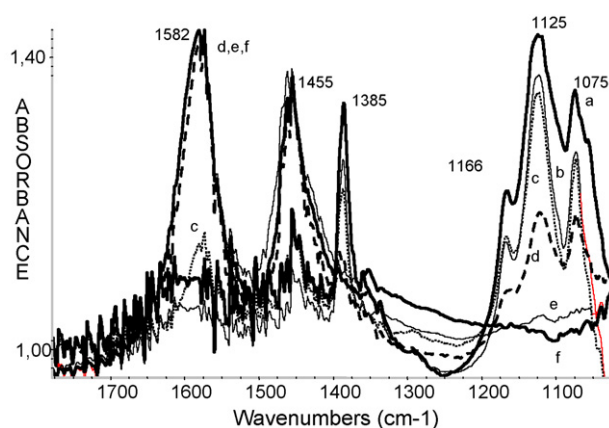


Fig. 10. FT-IR subtraction spectra of the adsorbed species arising from ethanol adsorption on MK1A-350 sample (a) adsorbed at r.t.; outgassed at (b) r.t., (c) 100 °C, (d) 150 °C, (e) 200 °C and (f) 250 °C.

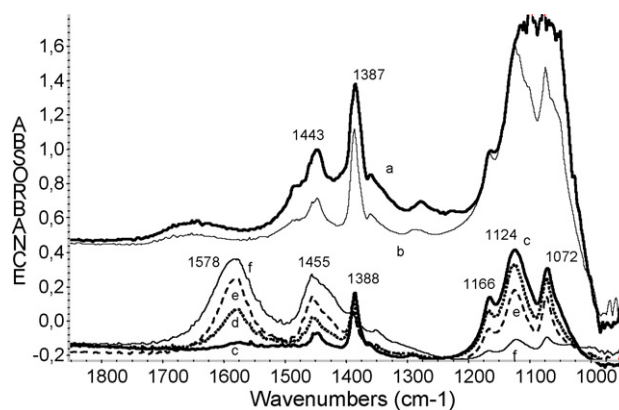


Fig. 11. FT-IR subtraction spectra of the adsorbed species arising from ethanol adsorption on MK2A-350 sample (a) adsorbed at r.t.; (b) outgassed at r.t., (c) 100 °C, (d) 150 °C, (e) 200 °C and (f) 250 °C.

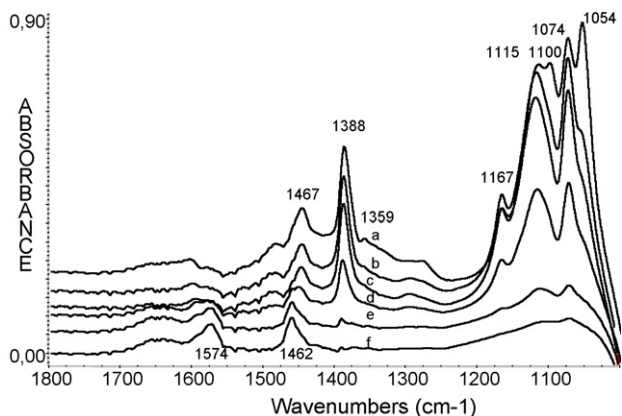


Fig. 12. FT-IR subtraction spectra of the adsorbed species arising from ethanol adsorption on Al_2O_3 pressed disks (a) at room temperature, (b) 150 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C and (f) 350 °C.

shifted upwards here, to near 1585 and 1455 cm^{-1} , with respect to 1560–1565 and 1425 cm^{-1} for the unsupported catalysts. In addition, the stabilities of these species are strongly enhanced with respect to the unsupported catalysts: ethoxides are still well evident after heating at 200 °C while acetates are evident even at 350 °C. This phenomenon can be in relation with the catalytic activity, which is far lower for supported catalysts. The light off is shifted up to 220–230 °C.

The spectra of the corresponding surface species on pure alumina are observed in Fig. 12. At RT the strong complex of bands in the 1200–1000 cm^{-1} region are evident due to coupled C–O and C–C stretchings. We can distinguish the bands of ethoxides at 1167 (weak), 1120, and 1075 cm^{-1} together with the corresponding CH deformation bands at 1447 and 1388 cm^{-1} (stable up to 300 °C), in agreement with the previous literature [26,27]. Undissociatively adsorbed ethanol is characterized by the band at 1060 cm^{-1} , and is almost totally desorbed (or dissociated) at 150 °C. The ethoxide bands disappear almost completely at 350 °C when weak bands at 1580 and 1470 cm^{-1} due to surface acetates are observed.

4. Conclusions

The comparison of the IR and the flow catalytic data, discussed above, allow us to propose some mechanistic features of the ethanol catalytic combustion process over Manganese-based catalysts.

The IR spectra show that ethanol adsorbs mainly in the form of ethoxides at the surface of the Mn-based combustion catalysts. Ethoxides convert to acetates when the catalytic conversion is lower than 20%, at 100 °C in the MK calcined at 350 °C and at 150 °C in the MK calcined at 500 °C. Acetaldehyde may be an intermediate in this reaction. On the other hand, at temperatures at which the conversion is almost complete (200 °C for the catalysts calcined at 350 °C and 250 °C for those calcined at 500 °C) acetates have already disappeared from the surface in the case of bulk manganese oxides.

The different stabilities of the surface acetates in the case of samples pretreated at 350 °C with respect to those pretreated at

500 °C may also be in relation to the catalytic activity. This relation supports the idea that acetates are actually intermediates rather than spectators in the catalytic oxidation of ethanol over bulk manganese oxides. The behaviour observed suggests that the evolution of acetates may be the rate-determining step of the catalytic combustion reaction. As a matter of fact, when catalytic activity becomes significant, “selective” oxidation at the C1 atom of ethanol to give aldehyde and acetate species appears to be a relatively fast step. It seems likely that the further combustion of acetates is very fast. In fact, no further intermediates can be observed after acetates.

A different situation is observed for the alumina-supported catalysts. The spectral features of ethoxides and acetates, which are also observed on supported catalysts, are very similar to those observed on alumina and quite different from those observed on bulk manganese oxides. However, the presence of manganese oxides on the alumina clearly weakens the stabilities of both ethoxides and acetates and strongly enhances the relative amount of acetates formed, with respect to pure alumina. In fact, alumina has a very weak catalytic activity and the main product of ethanol conversion is ethylene by dehydration, in contrast to the almost total selectivity to CO_2 found on manganese-based catalysts. On the other hand, acetates are still present at the surface of Al-supported catalysts even at 250 °C when conversion of ethanol is complete. This indicates that at least part of acetate species are not intermediates of ethanol combustion over alumina-supported catalysts. It seems likely that two types of adsorption sites exist in the case of alumina supported manganese catalysts. Some of them essentially reflect the catalytic activity of manganese oxides, although they are weakened by the interaction of alumina, while the others are essentially those of bare alumina, i.e. inactive in the catalytic oxidation. Part of acetate species in the case of Mn-alumina catalysts are consequently inactive spectators.

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