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Characterization and hydrocarbon oxidation activity of coprecipitated mixed oxides Mn_3O_4/Al_2O_3

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Abstract

The surface and redox properties of the manganese oxides Mn_3O_4 (hausmannite), Mn_2O_3 (bixbyite) and MnO_2 (pyrolusite) and of coprecipitated manganese aluminum Mn_3O_4/Al_2O_3 mixed oxide catalysts have been investigated by FT-IR spectroscopy of adsorbed probe molecules methanol and pyridine. Methoxy groups interacting with Mn^{3+}, Mn^{2+} and Al^{3+} cations are well distinguishable with respect to the position of their C–O stretching band. The evolution of methoxy groups to formate species allows to obtain information on the reducibility of the surfaces. Also pyridine allows to distinguish such sites and to evaluate their surface acidity. The results concerning the catalytic oxidation of propane over these materials are discussed in relation to their surface properties. The effect of bulk oxygen diffusion rate on the catalytic oxidation rate is evident.

Keywords: Mn_3O_4/Al_2O_3; FT-IR spectroscopy; Oxidation catalysts

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1. Introduction

Transitional aluminas have a prominent role in the field of heterogeneous catalysis, both as catalysts (e.g. for the Claus reaction [1]), and as supports (e.g. for hydrodesulfurization [2]). Many research groups published IR spectroscopic studies concerning the surface properties of aluminas [3]. In particular, Lavalley and co-workers [4–6] applied this technique to the adsorption of alcohols to better characterize the surface properties of this family of solids. The IR study of methanol adsorption has been later proposed by Lavalley as a general method to have information on the surface structures of the metal oxides. In the case of alumina, the interaction of methanol and deuterated methanol, with the subsequent formation of adsorbed methoxy species, has been extensively studied by IR spectroscopy and by microcalorimetry [7]. The adsorption of methanol at the catalyst surface is also a very useful method of investigation of the surface characteristics for other simple oxides, i.e. cerium oxide-based catalysts [8,9], zirconia [10–14], thoria [15] and for the study of mixed oxide such as ceria–zirconia [16,17]. Methanol dissociative adsorption over these surfaces allows to discriminate the adsorbed on-top or bridged methoxy species over different surface sites by studying the C–O stretching region of the IR spectrum. Moreover, in Ce-containing mixed oxides, the IR study of adsorbed methoxy species allows also the investigation of catalyst reduction [18,19] and reoxidation properties (the so-called oxygen storage capacity) following the relative intensities of the IR bands [20].

Mn oxides were found to be very active catalysts for the combustion of some organic compounds [21–24]. The oxidation/reduction behavior of pure manganese

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oxide in the presence of methane has also been investigated for its possible application as an oxygen storage material [25] (comparable to cerium oxide [26]) for a three-way catalyst.

Manganese–aluminum mixed oxides present an increased mechanic resistance with respect to the pure Mn oxide and an increased resistance to overheating [27]. In previous studies, we also found that pure Mn_3O_4 and alumina-supported manganese oxides show some interesting properties as propane oxydehydrogenation catalysts [28]. In order to have more information on the surface characters and on the oxidation power of manganese–aluminum coprecipitated mixed oxides; we present here the results of a study of their surface chemistry and of their catalytic activity in propane oxidation.

2. Experimental

Mn–Al samples were prepared by dissolving $Al(NO_3)_3 \cdot 9H_2O$ and $(CH_3COO)_2Mn \cdot 4H_2O$ in water. Precipitation of pure compounds and coprecipitation of Mn–Al catalyst with atomic ratio 2:1 (M2A1), 1:1 (M1A1) e 1:2 (M1A2) were obtained by rising the pH up to 9.5 with NH_3 and ageing the mixture 24 h at 333 K. After separation by centrifugation, the catalyst were dried at 383 K and calcined at 723 K. Pure oxides Mn_3O_4 (hausmannite) and Mn_2O_3 (bixbyite) preparation was described elsewhere [22,23]. MnO_2 (pyrolusite) was from C. Erba. Some characteristics of the samples are reported in Table 1.

IR spectra were recorded using a Nicolet Magna 750 and an IR cell connected to a conventional gas-manipulation apparatus allowing the introduction of probe molecules and the study of their evolution at increasing temperatures. All the samples (pure powder pressed disks) have been activated through heating in air at 673 K and following rapid evacuation (10^{-4} Torr) at 673 K. Reduction of the samples (where indicated) has been obtained by cycles of heating in hydrogen (400 Torr) followed by evacuation at the same temperature (673 K).

Catalytic tests were carried out in a continuous flow tubular reactor filled with 0.1–0.2 g of the sample mixed with inert material. The total gas flow was 350 cm^3/min and the partial pressures of HC, O_2 and He were 0.02, 0.12 and 0.86 atm, respectively, thus corresponding to an oxygen excess with respect to the total oxidation conditions.

3. Results

3.1. Catalysts characterization

Fig. 1 shows the spectra of the activated samples before adsorption experiments. No isolated OH stretching bands are found in the spectrum of Mn_3O_4 in the high frequency region after evacuation at 673 K, while in the low frequency region two well-defined bands are evident at 975 and 843 cm^{-1}. These bands fall in the wavenumber range typical of the surface cation–oxygen vibration bands [29], or, alternatively, are due to overtones of bulk vibrations. Their intensity lowered upon reducing thermal treatments but these bands do not disappear or shift significantly after adsorption of probe molecules. They can consequently be assigned confidently to overtone modes of bulk Mn–O stretchings of Mn_3O_4.

Other features in the region 1600–1300 cm^{-1} are due to surface carbonate species, while the intense

Table 1
Characteristic of the samples under study

Catalyst	Surface area (m^2/g)	Measured atomic ratio, Mn/Al	XRD
Mn_3O_4	24	∞	α-Mn_3O_4 (hausmannite)
M2A1	64	1.85	α-Mn_3O_4 (hausmannite)
M1A1	106	0.89	α-Mn_3O_4, α-Mn_2O_3, γ-Al_2O_3
M1A2	92	0.51	α-Mn_2O_3, Mn_5O_8, γ-Al_2O_3
Al_2O_3	70	0	γ-Al_2O_3
Mn_2O_3	9	∞	α-Mn_2O_3 (bixbyite)
MnO_2	15	∞	MnO_2 (pyrolusite)

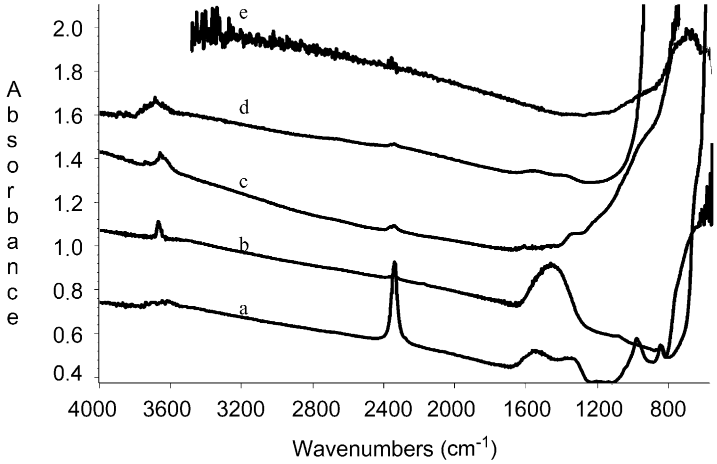

Fig. 1. FT-IR spectra of the activated surface of oxidized Mn_3O_4 sample (a), reduced Mn_3O_4 sample (b), of Mn_2O_3 (c), of M1A1 (d) and of MnO_2 (e). The spectra have been recorded at room temperature after evacuation at 673 K.

and strong band at 2338 cm^{-1} is assigned to trapped CO_2. Two weak bands at 3704 and 3609 cm^{-1} are not assignable to OH stretchings, but considering the intensity of the band of CO_2, they can be due to the combination of Fermi resonance doublet at 1388 and 1286 cm^{-1} of adsorbed CO_2 (masked by carbonate bands) with the fundamental at 2338 cm^{-1}.

Reduction of the surface, subsequent to the heating at 673 K in hydrogen, results in an improved transmission of the IR radiation (Fig. 1b), and in the disappearance of the two structural bands at 975 and 843 cm^{-1}, substituted by a weak doublet at 863 and 831 cm^{-1}. Interestingly, these two bands can be restored by high temperature oxidation in the presence of molecular oxygen (partial pressure of 100 Torr) only at temperature above 473 K. At 573 K they are completely recovered, showing (as for some other oxidation catalysts [30]) the possibility to obtain in the IR cell a redox cycle. Another effect of the reduction is the appearance of a sharp band at 3677 cm^{-1}, due to a stretching mode of an isolated OH, and not evident in the spectrum of the activated sample.

The spectrum of Mn_2O_3 pure powder activated at 673 K (Fig. 1c) presents two weak absorptions in the OH stretching region centered at 3744 and 3660 cm^{-1} (with a shoulder at 3641 cm^{-1}) while in the low frequency region the disk absorption is increasing continuously up to 600 cm^{-1}, the cut-off limit. In this frequency range, it is possible to detect some shoulders centered at 1320, 1100 and 940 cm^{-1} and a maximum at 676 cm^{-1}. These bands are not present in the skeletal spectrum and can be due to overtone modes. None of these features are detected for the MnO_2 sample (Fig. 1e); the IR transmission of this sample is quite low and does not allow us to discriminate different OH groups. Fig. 1d corresponds to the spectrum of the A1M1 mixed sample: in the low frequency region bands due to adsorbed carbonate species are detected. The study of the OH stretching region indicates that alumina OH groups are present, even if broadened by the manganese oxide incorporation.

3.2. Methanol adsorption over pure and mixed Mn oxides

The infrared spectrum of the adsorbed methanol over Mn_3O_4 (in Fig. 2a) shows two main bands in the C–O stretching region at 1069 and 1037 cm^{-1}, with a weak but complex component at 1440 cm^{-1}, due to the CH_3 deformation. These bands correspond to methoxy groups due to methanol dissociative adsorption on the sample surface and their attribution will be discussed in the following section. Moreover, we observe a broad OH stretching band near 3450 cm^{-1} which can indicate the presence of the undissociated H-bonded alcohol even after 10 min of evacuation at room temperature thus the presence of a species hydrogen-bonded through its own hydroxy

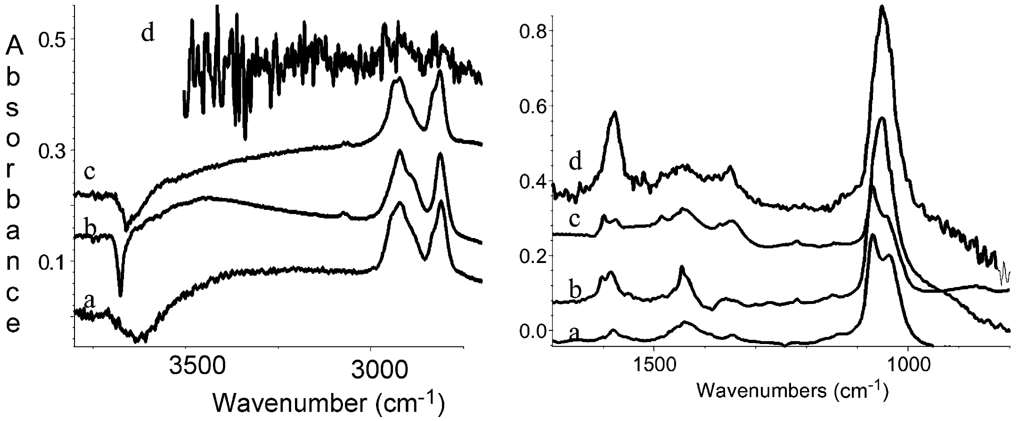

Fig. 2. FT-IR spectra of the surface species arising from methanol adsorption and evacuation at room temperature over oxidized Mn_3O_4 (a), reduced Mn_3O_4 (b), Mn_2O_3 (c) and MnO_2 (d).

group. The spectrum from methanol adsorption over the reduced surface (Fig. 2b) shows two split bands at 1069 and 1041 cm^{-1} (C–O stretching), the last appearing now as a shoulder. Traces of formate species (see the following section) formed from methoxides oxidation are found at temperature slightly higher than room temperature. The spectrum of methoxy groups is similar to the one resulting from the interaction of methanol with the oxidized sample followed by heating at 373 K, thus typical of a surface that has intermediate oxidation state (at 373 K the reactant methanol is partially oxidized and consequently the surface is partially reduced).

The spectrum of methanol adsorbed over Mn_2O_3 (bixbyite) at room temperature (Fig. 2c) is very different with respect to the one recorded over the spinel oxide. In this case, one main band centered at 1051 cm^{-1} is due to a C–O stretching of adsorbed methoxy species, while two weak shoulders appear at 1070 and 1030 cm^{-1}, very close to the bands observed in the spectrum of methanol over Mn_3O_4.

The spectrum resulting from methanol adsorption over manganese dioxide (Fig. 2d) shows a complex band in the C–O stretching region, that can be roughly resolved into two components at 1056 and 1044 cm^{-1}, assigned to νCO of terminal and bridged CH_3O– groups. Over this surface, carboxylate species (formate) are already formed after contact with methanol for 10 min at room temperature as revealed by bands at 1575 and 1350 cm^{-1}. These bands are slightly shifted at 1580 and 1358 cm^{-1} after following heating at 373 K. Carboxylate species are thought to be formed at the expense of adsorbed methoxides, as it will be discussed below.

Methanol adsorption is dissociative also on the mixed oxides, so we find in the CO stretching region at least two bands due to C–O stretching of methoxy species. The spectrum of the alkoxy species adsorbed at room temperature over the mixed oxides presents different IR features in the range 1100–1000 cm^{-1} with respect to the bands of the pure sample. In Table 2, the frequencies of the adsorbed species are summarized.

The spectra of the adsorbed species arising from contact of methanol with the MA mixed samples are reported in Fig. 3. From the analysis of the C–O stretching region, we tentatively discriminate the methoxy species adsorbed over Mn and Al ions. At the surface of the M2A1 (Fig. 3b) sample it is possible to observe bands at 1188 (rocking CH_3), 1096 and 1031 cm^{-1} (C–O stretching). The main bands at the higher frequencies are very close to the spectrum observed after methanol adsorption over pure Al_2O_3 [7] but the band at 1030 cm^{-1} is also present in the spectrum of the species adsorbed over Mn_3O_4. As for the sample M1A1 (Fig. 3c) it is still possible to notice the band at 1069 cm^{-1}, typical of methoxy species over Mn ions, and present here as a shoulder. We considered also the spectra corresponding to the subtraction [bands of methoxy species over mixed sample] – [bands of methoxy species over pure Mn_3O_4] (not reported in the figure) in which it

Table 2
Wavenumbers of methanol adsorbed over oxides at room temperature

Ass.	CH_3OH solution	Methoxy groups						
		Adsorption on γ-Al_2O_3	Adsorption on M1A2	Adsorption on M1A1	Adsorption on M2A1	Adsorption on Mn_3O_4	Adsorption on Mn_2O_3	Adsorption on MnO_2
νOH	3645	–	–	–	–	–	–	–
$\nu_{as}CH_3$	2977	2951		2940	2945	2960 sh	2930	
						2925		
ν_sCH_3	2838	2846		2820	2820	2830 sh	2814	
	2830	2823				2816		
$\delta_{as}CH_3$	1460			1456	1455	1455		
δ_sCH_3	1440		1440	1438	1440	1440		
δOH	1330	–	–	–	–	–	–	–
rCH_3	1068	1190	1187	1188	1188			
νCO	1029	1095	1099	1096	1096			
				1066 sh	1066 vw	1069	1051	1056
		1035 sh	1039	1037	1031	1037	1035 sh	1044

is possible to notice that the bands corresponding to the C–O stretching of methoxy species adsorbed over pure alumina are present on the mixed oxides while bands due to adsorbed methoxy species over pure manganese oxide are detectable as negative features. The analysis of this region of the spectrum indicates the presence of methoxy species adsorbed over manganese and over aluminum ions but we do not have evidence of methoxy species bridged over both ions.

The band at 1188 cm^{-1}, assigned above to a CH_3 deformation, is detectable only in mixed MA samples and on pure Al_2O_3 [7]. In the high frequency region, the spectrum of methoxy species on pure manganese oxide shows two main and complex bands centered at 2925 and 2816 cm^{-1} due to CH stretchings of the adsorbed CH_3O^- group. The same IR features are detected in the spectra of methoxy adsorbed on the mixed samples: bands position are only slightly shifted towards higher frequencies.

3.3. Thermal evolution of the adsorbed species

Over pure manganese oxide outgassing at 373 K causes only partial decrease of the bands at 1069 and 1037 cm^{-1}, showing that the alkoxy species is still stable at the surface, and the total disappearance of the

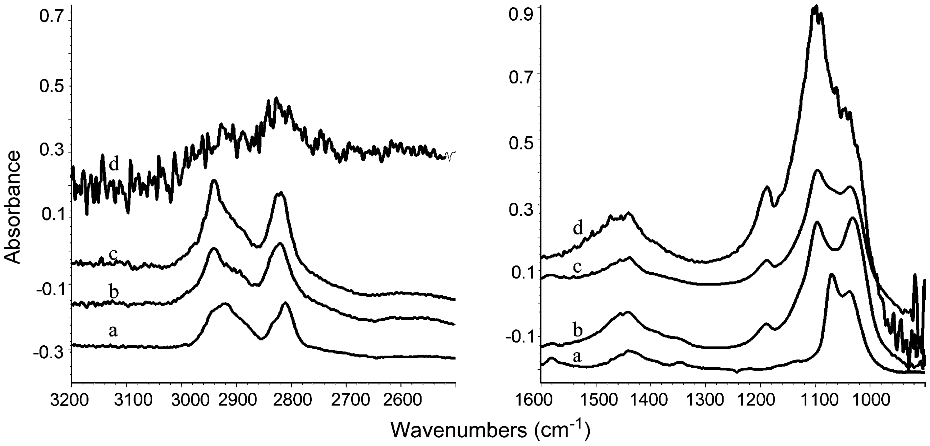

Fig. 3. FT-IR spectra of the surface species arising from methanol adsorption and evacuation at room temperature over pure Mn_3O_4 sample (a), over M2A1 (b), over M1A1 (c) and over M1A2 (d).

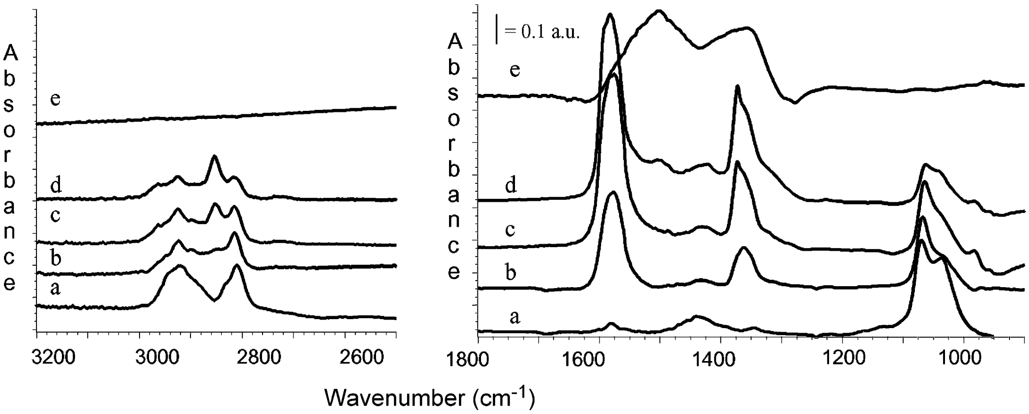

Fig. 4. FT-IR spectra of the surface species arising from methanol adsorption and evacuation over pure Mn_3O_4 sample at room temperature (a), at 373 K (b), at 423 K (c), at 473 K (d) and at 573 K (e).

band due to undissociated alcohol. New bands appear at 1575 and 1370 cm^{-1} (complex), typically assigned to the antisymmetric and symmetric COO– stretching with the CH deformation of the adsorbed formate species (Fig. 4) [31]. Actually, the bands due to the symmetric COO– stretching and the CH deformation are not resolved.

By increasing the temperature these two bands become more intense, reaching a maximum at 523 K, and split into several components at 1580, 1575, 1372 and 1360 cm^{-1}. Also in the high frequency region, the spectra are significantly changed by heating. At room temperature it is possible to observe two complex bands centered at 2920 and 2810 cm^{-1} ($\nu_{as}CH_3$, and $\nu_s CH_3$, respectively) with shoulders at 2900 and 2820 cm^{-1} (likely due to unresolved contribution of bridging and physisorbed species). At 473 K (Fig. 4d) IR features are almost completely changed and we can observe bands at 2964, 2925, 2854 and 2817 cm^{-1}, with a weak band near 2740 cm^{-1}. Most of these bands are due to formate species whose C–H stretching is multiply split due to multiple Fermi resonances [32]. Between 473 and 573 K (Fig. 4e), the adsorbed organic species completely disappear, probably because they decompose into CO_x and water, leaving at the surface carbonate species.

For methoxy species adsorbed over mixed oxides, the intensity of the band centered near 1030 cm^{-1} decreases upon heating. At 473 K, methoxy species are mainly oxidized to formate species (Fig. 5) characterized by bands at 1620 (shoulder) and 1594 cm^{-1} due to the COO– asymmetric stretching, at 1395 cm^{-1} (shoulder) due to the CH deformation, and at 1375 cm^{-1} due to the COO– symmetric stretching. The spectra reported in Fig. 5 are in fact completely consistent with the spectra of formate adsorbed over the same surfaces together with features due to residual methoxy species.

The splitting of the highest frequency band is evident in the spectra of the formate adsorbed on the mixed oxide, even more pronounced in the sample M2A1 (Fig. 5b) and can be due to the presence of two different formate species adsorbed over two sites at the surface. In any case, the position of the bands due to adsorbed formate species is significantly shifted towards higher wavenumbers with respect to the position of the same IR bands observed in the spectrum of these carboxylate species adsorbed over pure Mn_3O_4 (Fig. 5a).

Comparison of the thermal evolution of the adsorbed species indicates that over pure manganese oxide formate species are significantly formed earlier, already at 373 K, and the corresponding IR bands are stronger with respect to the same bands detected at 373 K over mixed oxides.

Over M2A1 sample formate species are already detectable at 373 K (Fig. 6) and the corresponding COO– antisymmetric stretching bands are split into two components assigned to formate species coordinated over Al and Mn ions. Formate species coordinated over aluminum ions (on pure alumina) are characterized by the asymmetric COO– stretching mode around

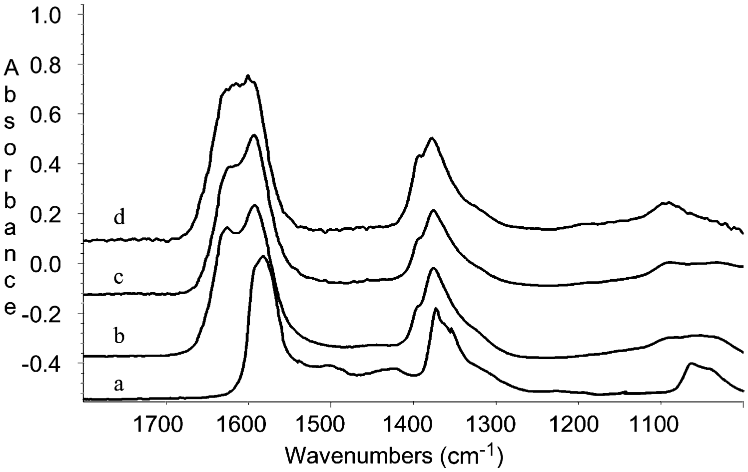

Fig. 5. FT-IR spectra of the surface species arising from methanol adsorption and evacuation at 473 K over pure Mn_3O_4 sample (a), over M2A1 (b), over M1A1 (c) and over M1A2 (d).

1630 cm^{-1} while formate bands around 1590 cm^{-1} are due to species adsorbed over Mn ions. Residual methoxy species, characterized by bands at 1188, 1096, 1070 and 1030 cm^{-1} (the last ones quite unresolved corresponding to the contribution of both Al and Mn adsorbed species) are still present at the surface up to 473 K (Fig. 6d). At higher temperatures the intensity of the band at lower frequency is decreasing faster than the component centered at 1096 cm^{-1}, due to the oxidation of methoxides over Mn ions. The oxidation process should be accompanied by the catalyst surface reduction [25] but in the spectrum the position of residual methoxy species bands is not significantly shifted to allow any further analysis. Thus, on mixed samples these species have been oxidized first over high oxidation number Mn ions, then the oxidized species formed could migrate both over residual high oxidation number Mn ions and over non-reducible Al ions.

Heating at 573 K (Fig. 6e) causes the disappearing of residual methoxy species and the almost complete decomposition of surface formate species. Also in this case the relative intensities of the asymmetric COO– stretching bands are inverted with respect to room

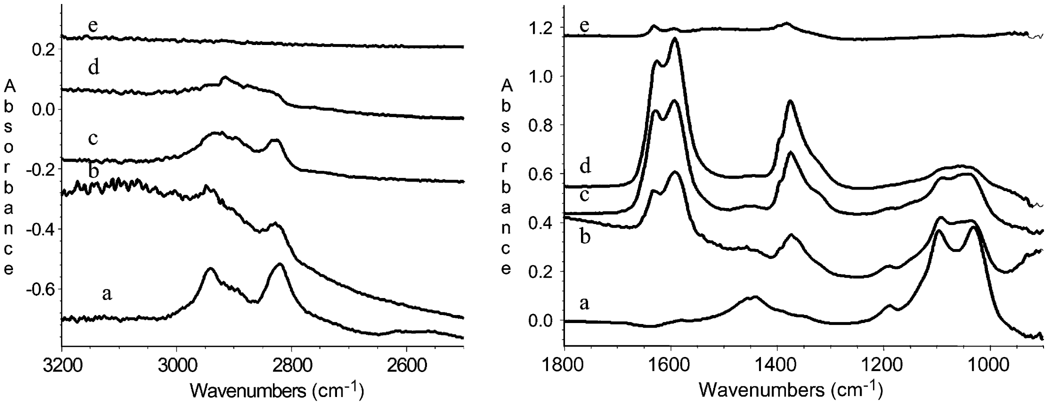

Fig. 6. FT-IR spectra of the surface species arising from methanol adsorption and evacuation over mixed M2A1 sample at room temperature (a), at 373 K (b), at 423 K (c), at 473 K (d) and at 573 K (e).

temperature: the high wavenumber component, associated to formate adsorbed over alumina (1630 cm^{-1}), is more evident. It seems likely there is a consumption of formate over oxidized Mn ions at 573 K while formate over Al ions are more stable resisting outgassing even at this temperature. The same effect is occurring over M1A1 and M1A2 samples. It is possible to discriminate bands due to formate adsorbed over different ions at increasing temperature.

Comparing Fig. 5b and c, it is possible to notice that apparently bands due to formate species adsorbed over alumina are stronger in the spectrum corresponding to the sample at higher Mn content, thus roughly indicating a segregation (or enrichment) of alumina at the surface of the Mn-rich sample. In this case, we are allowed to conclude that the surface composition of this mixed sample does not correspond to the bulk composition.

In the high frequency region bands due to methoxy species CH stretchings are present up to 473 K, while bands due to formate species are very weak and probably masked by the stronger adsorption.

Outgassing the mixed sample at high temperature causes the decrease of the broad band due to bonded OHs in the high frequency region and the disappearing of the complex negative bands around 3700 cm^{-1} due to alumina OHs perturbation, restoring an almost dehydroxylated surface.

3.4. Pyridine adsorption over pure and mixed manganese oxides

In Fig. 7, the spectra of pyridine adsorbed over reduced (Fig. 7a) and oxidized (Fig. 7b) Mn_3O_4 are reported. The 8a vibrational mode presents two main IR components at 1597 cm^{-1} with a pronounced shoulder around 1605 cm^{-1} due to pyridine coordinated over Lewis sites (pyridine interacting with Mn$^{3+/2+}$ ions). A band due to H-bonded pyridine can also contribute to the former one. All these bands are stable upon evacuation for 30 min at room temperature and upon increasing temperature, up to 373 K. Starting from 373 K the spectra present the features typical of transformation (oxidation) products. Pyridine oxidation is almost complete at 573 K, temperature at which the IR spectrum is completely changed; the aromatic ring is destroyed and it is possible to detect the formation of CO or, more likely, of CN$^-$ anions (bands in the 2230–2180 cm^{-1} region). No Brønsted acidity is detectable and Lewis acidity is definitely lower than on other oxides like Fe_2O_3 [33].

The spectrum of pyridine adsorbed over the reduced catalyst surface shows similar features described above (Fig. 7a). However, the 8a band is centered at 1600 cm^{-1}, without the component at lower frequencies, thus detecting at the surface only one species of Lewis site. In the high frequencies region pyridine

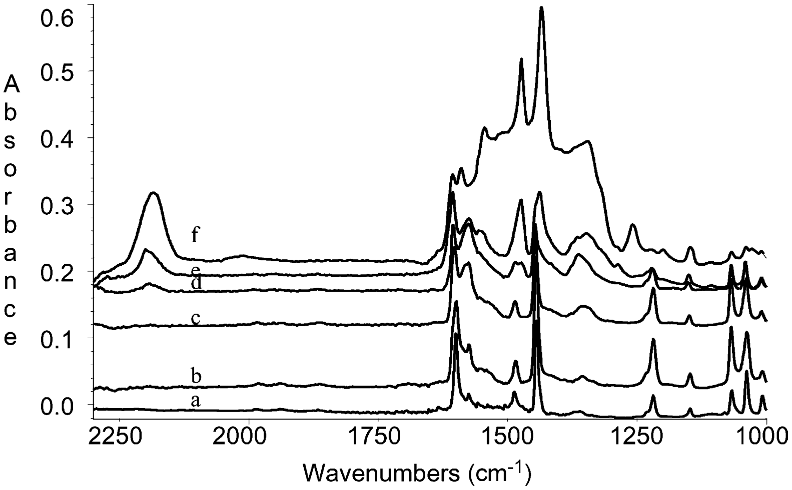

Fig. 7. FT-IR spectra of surface species arising from pyridine adsorption and evacuation at room temperature over reduced Mn_3O_4 (a) and oxidized Mn_3O_4 sample (b). The spectrum of the corresponding activated surface has been subtracted for each sample.

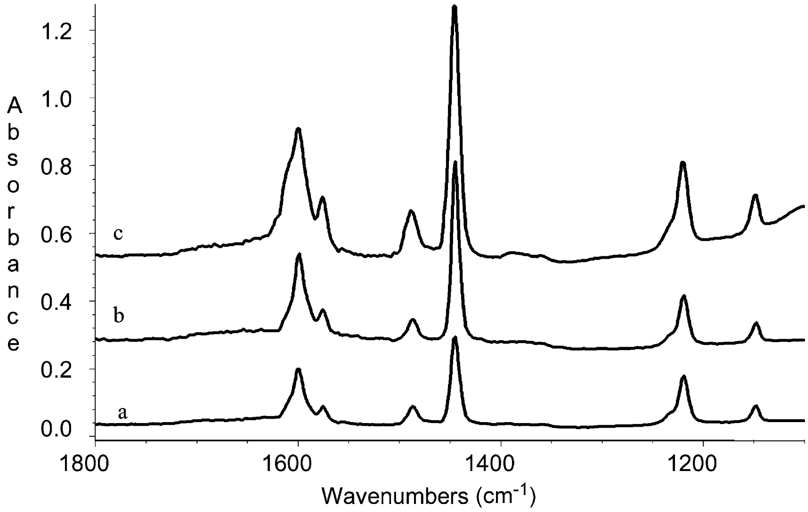

Fig. 8. FT-IR spectra of surface species arising from pyridine adsorption and evacuation at room temperature over M2A1 (a), over M1A1 (b) and over M1A2 (c). The spectrum of the corresponding activated surface has been subtracted for each sample.

adsorption causes the disappearance of the sharp band at 3677 cm^{-1} due to the isolated OH of the reduced sample, while a new broad band due to bonded OHs appears, centered at about 3500 cm^{-1} and with a shoulder at lower frequencies.

The spectra of pyridine adsorbed and outgassed at room temperature over mixed Mn/Al samples are compared in Fig. 8. The spectra closely correspond, taking into account the band position, however, there are significant differences concerning the band shape. In the spectrum of pyridine adsorbed over the sample M1A2 (Fig. 8c), the 8a band is more complex with respect to the corresponding band in the spectrum of pyridine adsorbed over pure manganese oxide and over Mn-rich samples and it is possible to detect the main maximum at 1599 cm^{-1} together with two component as shoulders at 1613 and 1620 cm^{-1}. The component near 1620 cm^{-1} is due to pyridine coordinated over tetrahedral aluminum ions (Al^{3+}) as reported on the Al_2O_3 spinel-type phases, while the band near 1613 cm^{-1} could be assigned to pyridine coordinated to sites near a cationic deficiency [34]. These components are even more resolved after outgassing at 423 K. Pyridine adsorption experiments confirm that Al^{3+} ions in a tetrahedral-like environment are present, at least at the surface of the Al-richest sample.

According to previous studies [35], the transmission of transitional alumina disks decreases above the cut-off limits upon pyridine adsorption, due to the relaxation of the surface metal–oxygen stretching modes. Under these conditions a complex negative band is detected in the subtraction spectrum weak and centered at about 850 cm^{-1} in the case of the Mn-rich samples, and at 950 cm^{-1} in the case of the M1A2 sample.

3.5. Catalytic oxidation activity

Propane and propene oxidation have been tested over both pure [2] and mixed manganese aluminum oxides (Figs. 9 and 10).

Propane total oxidation in the excess of oxygen occurs over pure manganese oxides at lower temperature than over mixed oxides. Propane conversion reaches 100% at 573 K over pure Mn_3O_4 while over M2A1 the conversion is completed only above 673 K. It is worth to note that the product distribution is completely different: over pure manganese oxide selectivity to CO_2 grows up until CO_2 is the only reaction product. Propene is formed at low propane conversion only. In the same experimental conditions over alumina-rich catalysts, propene and CO are formed and selectivity to CO stays at 3–5% even at high temperatures. The catalytic activity is decreased by alumina addition: over the sample Mn:Al 2:1 propene total conversion is still not attained on

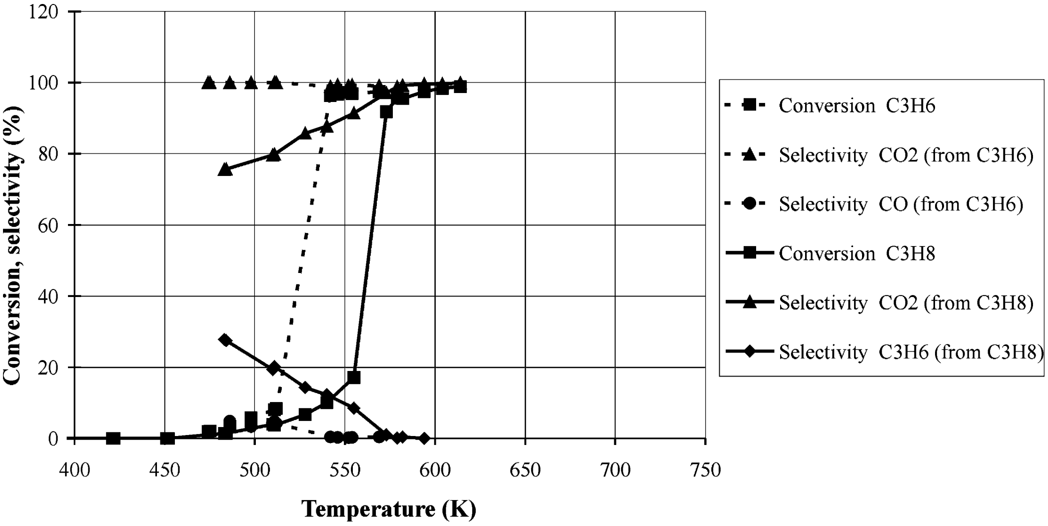

Fig. 9. Conversion of propane and propene and products selectivities on pure Mn_3O_4 in total oxidation conditions (oxygen excess).

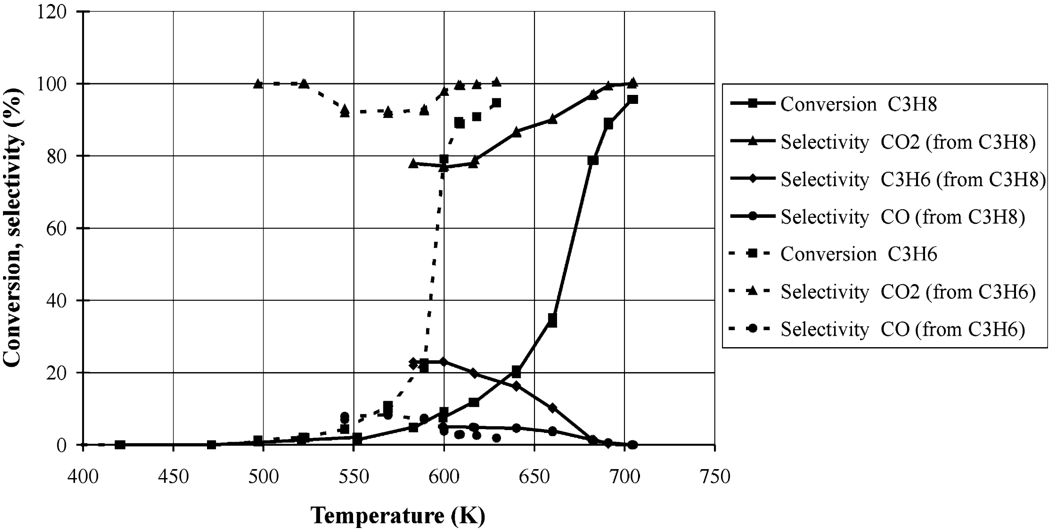

Fig. 10. Conversion of propane and propene and products selectivities on M2A1 sample in total oxidation conditions (oxygen excess).

the mixed oxide at 700 K in stoichiometric conditions and even by lowering contact time (both by lowering catalyst weight or increasing total flow). We can also observe some variations in the products selectivities: CO is produced in non-negligible amounts from propene oxidation on the mixed oxide, unlike on the pure oxide. CO production is only slightly higher, with respect to CO_2, from propene than from propane.

4. Discussion

Methanol adsorption over pure and supported manganese oxides is mainly dissociative, thus it is possible to use methoxy surface species as a probe to study the surface composition and the oxidation state of the cations.

The spectrum of methoxy species adsorbed over the spinel Mn_3O_4 is more complex than that arising from methanol adsorption over Mn_2O_3 and MnO_2 oxides, thus indicating an interaction between Mn ions at different oxidation states, revealed by methanol probe adsorption. The spectrum of the methoxy species over a reduced surface indicates that methoxy species coordinate always the same Mn ions (II and III), but the reduced intensity of the band at $1040\,cm^{-1}$ can be due to a reduced number of sites at high oxidation number. During methanol oxidation to formate species, we detect the weakening of the very same band. The overall picture suggests that under reducing conditions methanol reveals a slight modification of the surface of Mn_3O_4, although two type of manganese sites, probably different for oxidation state (Mn^{3+} or Mn^{2+}) are still present.

To rationalize the picture it seems possible to assign the band near $1070\,cm^{-1}$, predominant on both oxidized and reduced Mn_3O_4, to terminal methoxy groups bonded to Mn^{2+} ions. This parallels the OH stretching spectrum of reduced Mn oxide, likely MnO, where a single band at $3677\,cm^{-1}$ assignable to terminal hydroxy groups bonded to Mn^{2+}, similar to what happens on other rock-salt type oxides, such as MgO, CoO, NiO.

Thus, also according to previous studies [15] in which the parallelism of methoxy/hydroxyl species is pointed out, it is possible to hypothesize that the bands near $1030\,cm^{-1}$, observed in the spectra of methoxy groups on Mn_3O_4 to species coordinated over Mn^{3+}. They could be bridging to justify the low frequency observed, in agreement with previous studies that suggested that bridging methoxides are characterized by lower C–O stretching frequencies with respect to terminal methoxides [8]. The band near $1050\,cm^{-1}$ observed for methoxides on both Mn_2O_3 and MnO_2 can be assigned to terminal methoxides on Mn^{3+}. In any case, the observation of a very similar spectrum for methoxides on Mn_2O_3 and MnO_2 suggests that the two surfaces are, after activation upon outgassing, very similar. This is not unlikely because of the instability of MnO_2 in the absence of oxygen. Alternatively, we can suppose that methoxides on Mn^{4+} are oxidized to formats (which are in fact detected immediately) already at room temperature.

Over mixed oxides, we can discriminate between methoxy species adsorbed both on Mn and Al ions, being the corresponding C–O stretching modes detectable at quite different wavenumbers (1069 and $1037\,cm^{-1}$ on Mn_3O_4 vs. $1096\,cm^{-1}$ on Al_2O_3). The spectra resulting from methanol adsorption over mixed samples show features due to both surface species even if bands due to methoxy on Al sites are very strong and partially hidden bands due to methoxy on Mn sites.

The lack of detection of new methoxy species IR features on mixed oxides can point out the absence of CH_3O– species bridged over the two (Al and Mn) ions.

Thus, the analysis of the spectra arising from methanol adsorption allows to have evidence of redox phenomena. Heating the Mn_3O_4 sample after methanol adsorption causes the oxidation of methoxy groups to formate species at the expense of Mn at higher oxidation number, so that there is a decrease in the intensity of the corresponding IR band at $1037\,cm^{-1}$. At 473 K, bands due to formates reach their maximum intensity, while the band at $1064\,cm^{-1}$ is still present, indicating the contemporary presence of residual methoxy groups. At 573 K no more organic species are present at the surface and there are typical features of carbonate species.

Mixed oxides show a reduced oxidation activity: at 573 K formate species are still present at the surface even in the sample at higher Mn content and the formation of carbonate species is hardly detectable, if any. IR bands due to formate species can also be used to study the different surface composition: the component of the COO– asymmetric stretching at higher wavenumbers ($1632\,cm^{-1}$) is due to formate adsorbed over Al ions and is also still detectable at higher temperatures. This band is due to COO– stretching of formate species likely formed at the expense of the oxidizing ions (manganese) which migrate over aluminum ions. Formate species coordinated on aluminum ions are more stable and are still detectable after outgassing up to 573 K.

On the same samples pyridine adsorption gives additional information on the acid strength of Mn ions and on their oxidation state and location at the surface. The data reported above also show that reduced Mn_3O_4, i.e. MnO, has Lewis acid sites with intermediate acidity with respect to the oxidized sample (8a band at 1605 vs. band at 1597 cm^{-1}). These bands can be assigned to pyridine species coordinated over Mn^{3+} and Mn^{2+}, respectively. They are well distinguished from Al^{3+} sites that adsorb pyridine species whose 8a band is at 1620 cm^{-1}.

On the other hand, FT-IR data reveal quite a slight modification of the nature of the surface sites of Mn oxide when it is mixed with alumina. The catalytic data provide evidence for an even stronger perturbation. In fact, over Mn oxides the conversion of both propane and propene starts at much lower temperature than over Mn–Al mixed oxides. Moreover, CO_2 is the only product at high conversion over pure Mn oxides while CO is the predominant product over Mn–Al mixed oxides. This suggests that the catalysis for hydrocarbons oxidations is not exclusively surface sensitive, but bulk effect have also much importance. It is reasonable to suggest that the rate of bulk oxide ion migration can have a prominent role in generating the redox properties of the surface and that Mn oxide particles give rise to less active surfaces when mixed with alumina particles just because of a bulk effect.

5. Conclusions

The main conclusions of this work are the following:

1. Methanol can be proposed as probe molecule for the study of the surface composition of manganese/alumina mixed oxides, through the different IR features in the CO stretching region. Also in the case of these mixed oxide-based catalysts it appears to be possible to apply methanol adsorption to the study of the surface oxidation state. It seems likely that Mn^{4+}, Mn^{3+} and Mn^{2+} surface cations can be distinguished because Mn^{4+} (if they exist at the solid vacuum interface) causes the oxidation of methoxy groups already at r.t., while methoxy groups on Mn^{3+} and Mn^{2+} are stable at r.t. and are characterized by C–O stretching bands near 1040 and 1070 cm^{-1}, respectively. This is an important consideration regarding a possible use of manganese oxides (especially the spinel $\mathrm{Mn}_3\mathrm{O}_4$) as an oxygen storage material. On the other hand, methoxy groups also allow to distinguish Mn cationic centers from Al^{3+} cationic centers in Mn–Al mixed oxides, where methoxy groups are characterized by νC–O at 1090 cm^{-1}.
2. The study of the oxidative evolution of methoxy species to formate and CO_x gives also the indication of a different oxidizing capacity of the single cationic sites on mixed oxides as well as of the pure Mn oxide sample with respect to the mixed samples.
3. Formate species coordinated over Al or Mn ions on the mixed oxides are also well distinguishable.
4. Pyridine adsorption can also discriminate the acidic characters of the different absorbing sites Al^{3+}, Mn^{3+} and Mn^{2+} as well as of the pure Mn oxide spinel, whose surface is weakly acidic, and of the mixed samples, where alumina introduces stronger Lewis acidity.
5. Mn-based oxides are very active materials in the oxidation of propane and propene in excess of oxygen but, still, the mixed catalyst is less active in total combustion, allowing high selectivities to CO and also higher productions of propene from propane. A bulk effect such as bulk oxygen diffusion should be the main responsible for the decrease in catalytic activity when Mn oxides are mixed with alumina.

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