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# The reactivity of a Fe–Ti–O mixed oxide under different atmospheres: study of the interaction with simple alcohol molecules

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## Abstract

In this paper, the interaction between simple alcohols (methanol to 1-butanol) and a Fe–Ti mixed oxide was investigated. The reactivity of the mixed system was studied both at atmospheric pressure and in vacuum conditions and compared with that of the pure oxides ( $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ ). To understand the influence of the oxygen presence in the reaction mixture, the reactivity was investigated both in inert gas as well as in oxygen atmosphere. X-ray photoelectron spectroscopy (XPS) and quadrupole mass spectrometry (QMS) have been used for the experiment in high vacuum (HV), while Fourier transform infrared spectroscopy (FTIR) and QMS have been used for the experiment in rough vacuum and under atmospheric pressure conditions. The characterisation of the sample by means of XPS, X-ray diffraction and IR spectroscopy preceded the reactivity study. When compared with  $\text{Fe}_2\text{O}_3$ , the Fe–Ti–O mixed oxide seems to be less reactive with respect to the alcohols; the interaction between alcohol and surface is mainly molecular, as in the case of  $\text{TiO}_2$ . Moreover, the oxidising power of the mixed oxide is lower than that of  $\text{Fe}_2\text{O}_3$  (only traces of carbonic compounds are evident). © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Chemisorption; Iron oxide; Titania; Alcohols; FTIR

## 1. Introduction

The catalytic properties of a multicomponent system may be strongly influenced by the composition and the preparation procedure. This signifies the possibility to tune the activity and/or selectivity of a catalyst by means of a convenient synthesis procedure or component choice. In previous papers, we studied the reac-

tivity of  $\text{Fe}_2\text{O}_3$  with respect to small organic molecules [1,2]. Hematite easily dissociates molecules characterised by a weak Brönsted acidity (such as methanol). Moreover, iron oxide had shown a great activity in the oxidation reactions. Methanol, for example, is oxidised to formate at temperatures higher than 400 K. The reactivity of  $\text{TiO}_2$  [3–17] is the subject of several papers because of its importance as a catalyst in photoassisted reactions [18–20]. Nevertheless, the literature results give ambiguous indications.

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A selection of mixed oxides interesting from a catalytic point of view cannot prescind from a detailed knowledge of their surface reactivity. The significant reactivity difference between  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  makes the study of the reactivity of Fe–Ti–O mixed oxides interesting. As a matter of fact, in multicomponent systems, the active sites (acid or basic sites or red–ox sites, for example) may be different with respect to those present on the pure oxides. This allows obtaining different reactivity as a function of the composition, the preparation procedure or eventual treatments.

The synthesis procedure can also be relevant to determine the surface reactivity of the catalyst: the wet impregnation method, as an example, allows to obtain supported oxides while with co-precipitation procedures, like in the present case, “bulk” mixtures can be obtained. In the case of mixed oxides obtained by impregnation methods, the choice of the supporting oxide can also be determinant for the crystallographic and chemical structure of the supported oxide and this may severely influence the reactivity of the mixed system.

This work is part of a comprehensive study aimed at the understanding of the reactivity of mixed iron and titanium oxides. We already reported the results obtained from chemisorbing small organic molecules on the pure iron oxide [1,2]. In the interaction between simple alcohols and hematite, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and quadrupole mass spectrometry (QMS) results show that both at atmospheric pressure and under HV conditions, methanol is chemisorbed dissociatively and molecularly. Dissociatively chemisorbed methanol is the main present species. Molecularly chemisorbed methanol was desorbed around 400 K, while methoxy groups were completely eliminated at 470–500 K. At temperatures higher than 400 K, the formation of formate species on the surface of the iron oxide is evident. Iron formate is not desorbed from the surface or decomposed even at a high temperature. The chemisorption of

higher alcohols on hematite is mainly molecular even if a small quantity of alkoxide is present. The dissociated form becomes more relevant with increasing temperature. The main chemisorption products are hydrocarbons.

In this paper, we present the results obtained considering the interaction between alcohol molecules and a Fe–Ti–O mixed oxide prepared by co-precipitation. Until now, only few works on Fe–Ti–O systems have been published and are mainly about the activity/selectivity of Fe–Ti–O powder as a function of the composition or the preparation conditions [21]. Our goal is to give a contribution to the comprehension of the mechanisms of interaction between small organic molecules and the mixed oxide system active sites which is of fundamental importance to reach a planning capacity in heterogeneous catalysis.

The reactivity of this mixed oxide was studied in two ways:

1. at atmospheric pressure and in rough vacuum by means of diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy;
2. in high vacuum (HV) with QMS and XPS.

In both cases, the experiments were carried out exposing the surface to alcohol vapours both in presence and in absence of oxygen to better investigate the influence of the oxygen presence on the reaction pattern. This influence may be particularly relevant in the HV conditions because in this case oxides may easily lose oxygen when kept at high temperatures. Moreover, oxygen can be an important reagent for oxidation reactions.

Methanol, ethanol, 1-propanol and 1-butanol have been chosen as probe molecules to evaluate the properties of this supported oxide. Methanol is an important probe to study the oxide reactivity because it shows an interesting reactivity that can change deeply as a function of the oxide [22,23]. Higher alcohol chemisorption is an important tool to study the acidic properties of the oxides and to understand de-

composition mechanisms of complex molecules, such as olefins (in fact, alkoxides are often important intermediates in olefin oxidation on oxides based catalysts and their reactivity and stability could be responsible for the reaction pattern and for the selectivity of the catalyst). With this purpose, new measures are in course.

The interaction between  $\text{TiO}_2$  and methanol has also been studied for comparison.

The reactivity of this mixed oxide is very different with respect to the reactivity of the pure  $\text{Fe}_2\text{O}_3$ . In this last case, methanol strongly interacted with the surface chemisorbing dissociatively while the interaction between methanol and the Fe–Ti–O surface was mainly molecular, as in the case of  $\text{TiO}_2$ . Molecularly chemisorbed methanol desorbs from the surface around 360–380 K while at higher temperatures (500–550 K) methoxy species decompose to water, hydrogen and carbon oxides. The formation of formaldehyde is also evident but the oxidising power of the mixed oxide is lower than in the case of  $\text{Fe}_2\text{O}_3$  (in that case, formate was a significant product).

The interaction between the higher alcohol and the Fe–Ti–O surface is slow and, essentially, molecular (only traces of alkoxy groups). At temperatures lower than 500–600 K, alcohols desorb and decompose to water and methane. Aldehyde desorption becomes significant at higher temperatures. When the chemisorption is carried out in absence of oxygen (HV experiment), a fragmentation reaction giving rise to hydrocarbons becomes important.

Mixed oxides with different Ti/Fe atomic ratio can show different reactivity and new experiments are in course.

## 2. Experimental

### 2.1. Catalyst preparation

The  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  catalysts were prepared [21] by hydrolysis of mixed solutions of ferric nitrate

and titanium tetrachloride in alkali ambient ( $\text{NH}_4\text{OH}$  1 M aqueous solution); titanium tetrachloride was obtained by dissolution of metallic titanium in acidic ambient (for hydrochloric acid).

The precipitate was suction filtered and washed, first by boiling water and then with cold water until the filtrate showed a pH = 7. The used water was twice distilled.

The filtrate was heated in air at 523 K for 12 h and then calcined (in air) at 773 K for 6 h. In both cases, the desired temperature was reached in 1 h. The  $\text{TiO}_2$  (99%) was from a commercial source (Carlo Erba).

The samples were prepared for the reaction in HV conditions by pressing the catalyst powders into a pellet; the pellet was pressed at 1000 psi for 20 min at room temperature (RT). Initial treatment of the samples included (i) evacuation at RT in UHV for 12 h, (ii) cleaning of the surface with annealing treatments (700 K, 30 min) in oxygen atmosphere ( $4 \times 10^4$  Pa) until the almost complete elimination of carbon is reached. Oxygen (99.998%) was used without further purification.

Several annealing treatments in oxygen have been done on the calcined powder (623 K) for FTIR analysis to eliminate humidity from the sample and until a stable IR spectrum as a function of the temperature has been obtained.

### 2.2. Reaction with the alcohols

The alcohols (HPLC grade) used in this study were from a commercial source (Sigma–Aldrich) and were used without further purification. In the reaction carried out in the HV chamber, the exposure of the pellet to the alcohol vapours was carried out at temperatures between RT and 723 K at a total pressure of ca.  $4 \times 10^{-4}$  Pa. The volatile products have been characterised, by means of a quadrupole gas analyser (HV), every 25 K. In the mass spectra, the contribution of the parent alcohol was subtracted [24] while the assignments have been

done by means of the fragmentation patterns [25]. The reported data have been obtained subtracting to the spectrum after chemisorption the spectrum obtained before.

The exposure in the FTIR equipment has been done using the COLLECTOR<sup>TM</sup> apparatus for DRIFT spectroscopy from Spectra-Tech. fitted with the high temperature high pressure (HTHP) chamber. The HTHP chamber was used at atmospheric pressure, fluxing nitrogen through a bubbler containing the alcohols. In the case of methanol, the HTHP chamber was connected to a quadrupole mass spectrometer (RIAL). The quadrupole inlet was maintained at  $10^{-3}$  Pa by means of a differential turbo pumping. In this case, the HTHP chamber was first evacuated and then directly filled with methanol vapours. After a prolonged time, the outlet toward the mass spectrometer was opened while the sample was heated from 300 to 700 K checking for the products every 25 K.

It must be remembered that between the experiment in HV and the experiment in the HTHP reactor, many significant differences are present. First of all, in the HV reactor, there is a strictly controlled atmosphere; on the contrary, in the HTHP reactor “real world” conditions are approached. Moreover, in the HV experiment methanol fluxes during the whole experiment and the contact time between reagents and surface and between products and surface may be different than in the HTHP reactor. It has to be considered that the photoelectron spectroscopies are surface specific techniques and than the XPS results may show significant differences with respect to those obtained from FTIR.

### 2.3. XPS measurements

XPS spectra were recorded using a Perkin Elmer PHI 5600ci spectrometer with a monochromatic Al-K $\alpha$  source (1486.6 eV) working at 300 W. The working pressure was less than  $1 \times 10^{-6}$  Pa. The spectrometer was calibrated assuming the binding energy (BE) of

the Au 4f<sub>7/2</sub> line at 84.0 eV with respect to the Fermi level. Extended spectra (survey) were collected in the range between 0 and 1250 eV (187.85 eV pass energy, 1 eV step, 0.05 s step<sup>-1</sup>). Detailed spectra were recorded for the following regions: C 1s, O 1s, Fe 2p, Ti 2p (11.75 eV pass energy, 0.1 eV step, 0.1 s step<sup>-1</sup>). The standard deviation in the BE values of the XPS lines is 0.1 eV. After a Shirley-type background subtraction [26], the raw spectra were fitted, when necessary, using a non-linear least square-fitting program adopting Gaussian–Lorentzian (for carbon and oxygen peaks) or Donjiac–Sunjic (for the iron peak) peak shapes [27]. The atomic composition was evaluated using the PHI sensitivity factors [28]. To take into consideration charging problems C 1s peak at 285.0 eV was considered and the peaks BE differences were evaluated. The temperature of the pellet has been evaluated by means of a thermocouple directly in contact with the sample-holder.

### 2.4. FTIR measurements

The IR spectra have been obtained by means of a Bruker IFS 66 spectrometer in the diffuse reflectance mode and displayed in the Kubelka–Munk Units [29,30]. The resolution of the spectra was 4 cm<sup>-1</sup>. The temperature of the powder has been checked by means of a thermocouple inserted into the sample-holder directly in contact with the powder.

### 2.5. AFM

All images were obtained on a Park Scientific Autoprobe CP instrument using non-contact AFM in air at RT. The adopted mode was the “constant force mode” (the force being around 1–2 nN). The cantilever used is a Park Scientific Instruments Ultralever 2  $\mu$ m: a gold-coated silicon cantilever with a silicon tip. The images are presented without any elaboration but background subtraction. The pellets (1000

psi for 20 min at RT) were glued to the AFM sample holder using a cyanoacrilate glue.

### 3. Results

#### 3.1. Catalysts characterisation

The AFM images obtained for the Fe–Ti–O catalysts show that the non-calcined sample was constituted by small particles aggregated to form a three-dimensional structure with cavities (Fig. 1a). After the calcination treatment, this structure becomes more compact and, around 823 K, a strong crystalline structure (Fig. 1b) appears. After the calcination at 773 K, the particles have a prolonged shape and their dimensions are of fractions of microns (Fig. 1c).

The XRD spectrum of the Fe–Ti–O mixed system shows peaks at different angles with respect to those of hematite and anatase, suggesting the presence of brookite or pseudobrookite [31].

The Ti  $2p_{3/2}$  and O 1s XPS peaks (Fig. 2) position in  $TiO_2$  (458.7 and 529.9 eV, respectively) are those expected for  $TiO_2$  [32,33]. The O/Ti atomic ratio (ca. 2.8) shows the presence of contamination and/or OH groups. This was confirmed by the O 1s peak shape showing a tail at the high BE side. The O/Ti atomic ratio and peak shapes do not change significantly after the annealing treatment in oxygen atmosphere; only the carbon contamination decreases markedly. This result suggests the difficulty to completely eliminate the Brönsted acidity from a  $TiO_2$  surface.

The XPS survey spectra obtained for the Fe–Ti–O mixed oxide show the presence of carbon and nitrogen; this last contaminant, in particular, is related to the preparation procedure.

In the Fe–Ti–O system, the Fe  $2p_{3/2}$  peak position (711.2 eV) and shape are characteristic of Fe(III) [36] (Fig. 3) while the Ti  $2p_{3/2}$  peak position (458.5 eV) indicates (Fig. 3) the pres-

ence of an oxidised form of titanium ( $TiO_2$  or titanate) [33].

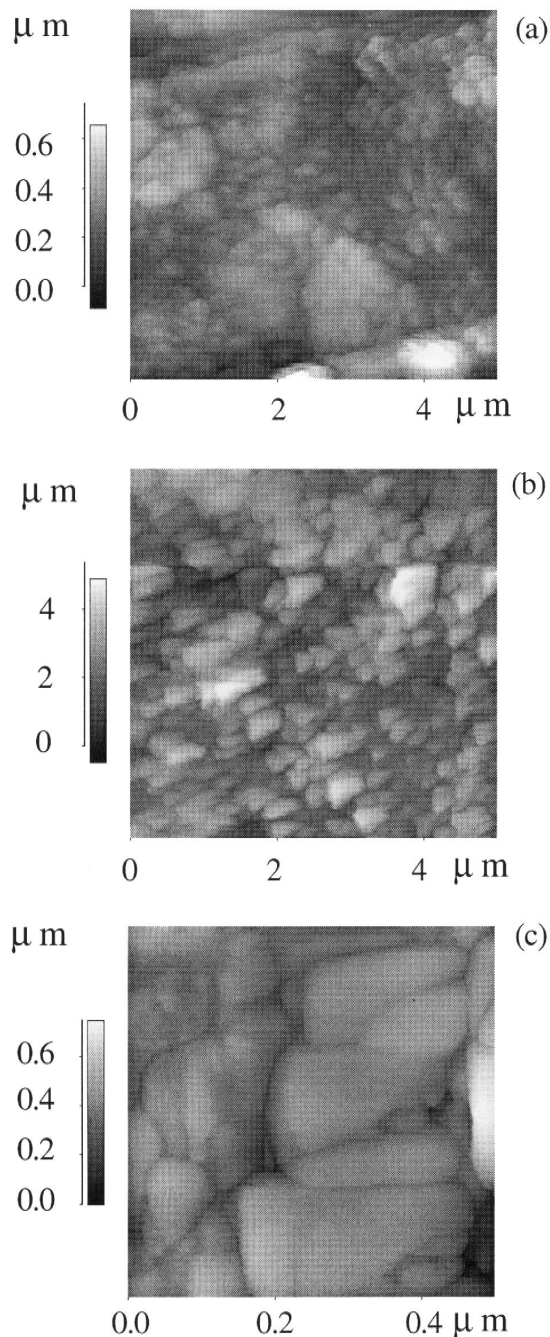


Fig. 1. AFM images of the Fe–Ti–O mixed oxide: (a) not calcined ( $5 \times 5 \mu m^2$ ); (b) calcined at 823 K ( $5 \times 5 \mu m^2$ ); (c) calcined at 773 K ( $0.5 \times 0.5 \mu m^2$ ).

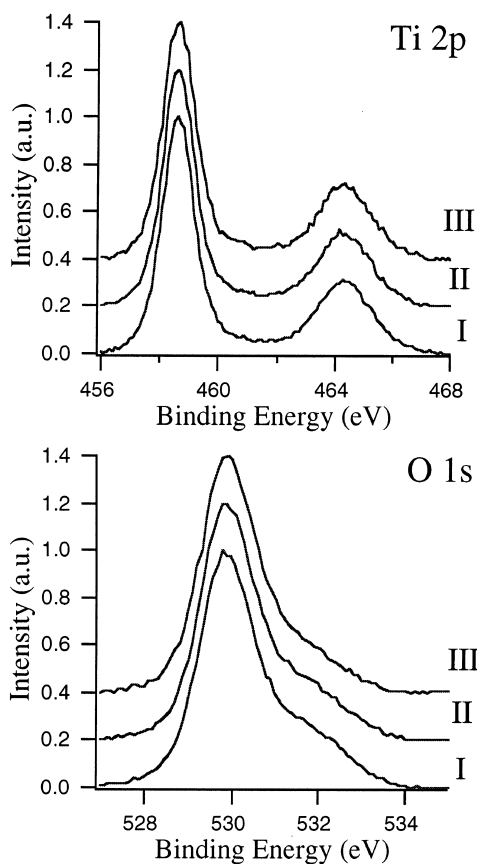


Fig. 2. XPS spectra obtained for the  $\text{TiO}_2$  before (I) and after the exposure to the methanol vapours at RT (II) and at 773 K (III).

O 1s peak (Fig. 3) is centred at 530.1 eV, a position typical for oxygen bonded to transition metal [34]. The Fe 2p and O 1s peak positions are in tune with the corresponding values obtained for the Fe–O system (710.9–711.2 and 529.5–530.0 eV, respectively).

In the samples not cleaned with the annealing treatment O 1s peak was always asymmetric with a tail on the high BE side; the fitting procedure shows the presence of additional contributions centred around 532 eV and corresponding to the presence of hydroxyl moieties. The high BE side tail is difficult to remove even with the annealing treatments. It has to be considered that, in contrast to the case of the  $\text{Fe}_2\text{O}_3$  surface, in this last case the OH groups, can be completely eliminated by a heating treatment (700 K) in oxygen atmosphere (10 Pa) [1,2].

The Fe–Ti–O system is very rich in oxygen: the Fe/(Fe + Ti) atomic ratio is 0.6 while the O/(Fe + Ti) atomic ratio is around 3.0. The

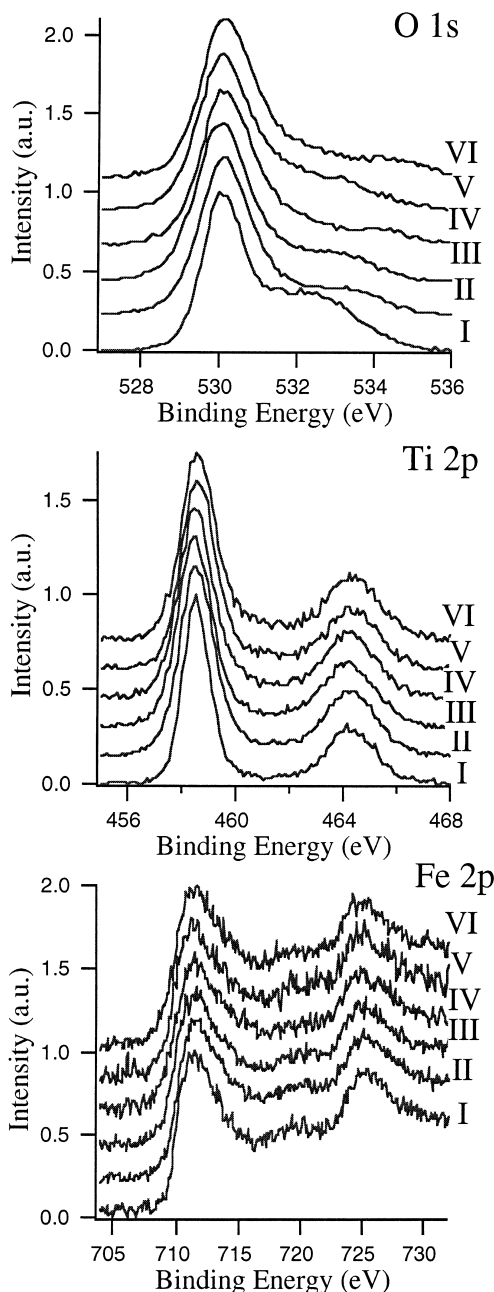


Fig. 3. XPS spectra of the Fe–Ti–O mixed oxide “as calcined” (I), after the annealing treatment in oxygen atmosphere (II), after the exposure to the alcohol vapours at RT (III) and at 773 K (IV); after the exposure to the alcohol + oxygen vapours at RT (V) and at 773 K (VI).

annealing in oxygen greatly reduces the contamination and modifies the Fe/(Fe + Ti) and O/(Fe + Ti) atomic ratios whose values after the treatment are 0.7 and 1.9, respectively. XPS data suggest that the calcination causes the surface segregation of titanium oxide. As a matter of fact, the Ti/Fe atomic ratio is 0.6 in the sample before the calcination, 0.7 after calcination at 773 K and 0.9 at 873 K. O/(Fe + Ti) atomic ratio keeps almost constant.

FTIR spectra obtained for the Fe–Ti–O system are shown in Fig. 4. The O–H stretching region (Fig. 4a and b) shows a broad band around  $3420\text{ cm}^{-1}$  with a shoulder at about  $3200\text{ cm}^{-1}$  that are due to the presence of water molecules H-bonded to the surface OH groups. At higher wavenumbers, a broad band around  $3670\text{--}3690\text{ cm}^{-1}$  seems to be composed of several contributions that decrease as a function of the temperature. The following contributions are visible around 700 K: 3670, 3715 and  $3750\text{ cm}^{-1}$ . The higher wavenumbers contributions are probably due to the isolated OH groups and it is reasonable to think that their contribution becomes evident as temperature increases (i.e., when water interacting with the surface OH groups desorbs). A comparison with the FTIR spectra obtained for the  $\text{Fe}_2\text{O}_3$  [1,2] shows, for the mixed system, a more intense contribution

around  $3670$  and  $3710\text{--}3720\text{ cm}^{-1}$ . Moreover, after the heating treatment in oxygen atmosphere, a peak around  $3630\text{ cm}^{-1}$  appears in the case of  $\text{Fe}_2\text{O}_3$  and not for the Fe–Ti–O system. The heating treatment causes the partial elimina-

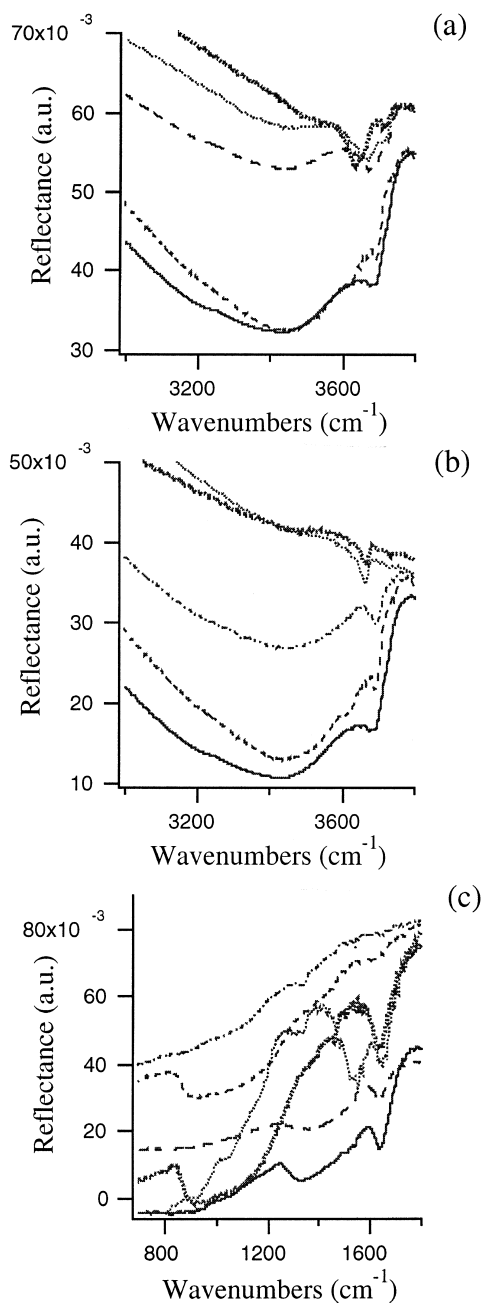


Fig. 4. FTIR spectra obtained for the mixed oxide before the exposure to the alcohol vapours; the corresponding spectra obtained for the pure oxide are also shown: (a) as calcined Fe–Ti–O (—), as calcined  $\text{Fe}_2\text{O}_3$  (---); Fe–Ti–O at 703 K in oxygen (.....), spectrum of the Fe–Ti–O obtained (at RT) after treatment with oxygen at 703 K (----); spectrum of the  $\text{Fe}_2\text{O}_3$  obtained (at RT) after treatment with oxygen at 703 K (|||||); O–H stretching region; (b) as calcined Fe–Ti–O (—), as calcined  $\text{TiO}_2$  (---), as calcined  $\text{Fe}_2\text{O}_3$  (---),  $\text{TiO}_2$  at 673 K in oxygen (.....), spectrum of the  $\text{TiO}_2$  obtained (at RT) after treatment with oxygen at 703 K (|||||); O–H stretching region; (c) as calcined Fe–Ti–O (—), as calcined  $\text{TiO}_2$  (|||||), as calcined  $\text{Fe}_2\text{O}_3$  (.....), spectrum of the Fe–Ti–O obtained (at RT) after treatment with oxygen at 703 K (----), spectrum of the  $\text{TiO}_2$  obtained (at RT) after treatment with oxygen at 703 K (---), spectrum of the  $\text{Fe}_2\text{O}_3$  obtained (at RT) after treatment with oxygen at 703 K (---);  $\text{H}_2\text{O}$  bending region.



tion of OH-groups and water molecules; this elimination is more difficult and reversible in the case of the mixed oxide.

The FTIR spectra of  $\text{TiO}_2$  (Fig. 4b) show a lower intensity in the O–H stretching region with respect to the corresponding spectra of  $\text{Fe}_2\text{O}_3$  and Fe–Ti–O. The main contributions observed in the “as calcined”  $\text{TiO}_2$  sample are centred around 3695 and 3450  $\text{cm}^{-1}$ . After the heating treatment (with and without oxygen), these bands disappeared and a new peak centred on 3665  $\text{cm}^{-1}$  appeared.

Griffiths and Rochester [17] observed, in the case of rutile, the presence of several contributions due to the stretching vibrations of OH groups: 3700 and 3680  $\text{cm}^{-1}$  (free OH groups), 3655, 3610 and 3520  $\text{cm}^{-1}$  (bonded OH groups). To loosely or tightly bonded water molecules are due a broad band at 3400  $\text{cm}^{-1}$  and a peak at 1620  $\text{cm}^{-1}$ . The FTIR results obtained by Griffiths and Rochester show that water molecules weakly held through hydrogen bonding interaction with surface OH groups disappear at low temperature (< 373 K). Strongly held water (bonded to Lewis acidic surface) is in part retained on the surface even after evacuation at 623 K.

Also, the region 800–1800  $\text{cm}^{-1}$  (Fig. 4c) shows remarkable differences between the three systems. The spectrum of the “as calcined”  $\text{Fe}_2\text{O}_3$  shows the presence of two intense peaks around ca. 1525 and 1640  $\text{cm}^{-1}$  (as well as a broad band around 1310–1320  $\text{cm}^{-1}$ ) while the corresponding  $\text{TiO}_2$  spectrum does not show any contribution in this region. The spectrum of the as calcined Fe–Ti–O mixed oxide shows a main peak around 1640  $\text{cm}^{-1}$  (as well as a broad band around 1330  $\text{cm}^{-1}$ ).

All these results suggest a different Brönsted acidity for these systems and the behaviour of the Fe–Ti–O mixed oxide cannot be considered as the combination of those corresponding to the pure oxides. It is our opinion that these differences can severely influence the surface reactivity and thus a more detailed investigation concerning the variation of the surface Brönsted

acidity as a function of the composition, preparation procedures and heating treatments is in course. In our opinion, the experimental work in

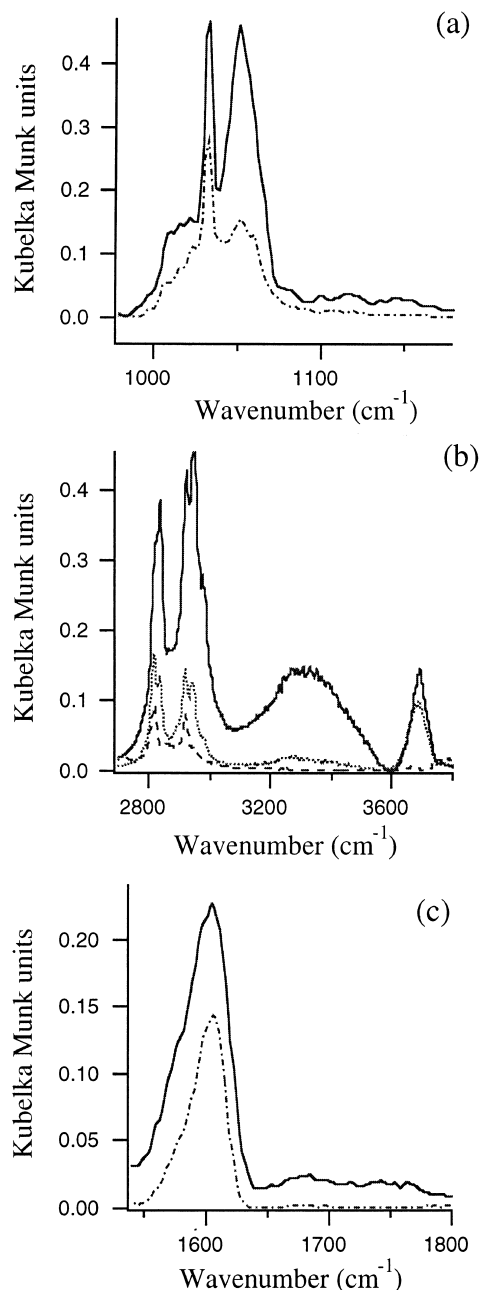


Fig. 5. FTIR spectra of methanol adsorbed on the Fe–Ti–O mixed oxide at atmospheric pressure and at different temperatures (— RT, - - - 323 K, ..... 353 K, - . - . 473 K): (a) C–O stretching region; (b) O–H and C–H stretching regions; (c) region between 1525 and 1800  $\text{cm}^{-1}$ .

progress in our laboratory will allow us to better clarify the mechanisms of acidity formation. As a preliminary consideration, the charge increase (i.e., the formation of Lewis acid sites) originated with the introduction of titanium in the iron oxide matrix can be considered. This charge increment induces the adsorption of hydroxyl groups on the Lewis acid sites with the creation of Brönsted acid sites.

### 3.2. Fe–Ti–O system

#### 3.2.1. Chemisorption of methanol at atmospheric pressure and in rough vacuum conditions

The FTIR spectra of the CH<sub>3</sub>OH adsorbed, at RT on the Fe–Ti–O powder are shown in Fig. 5. In Table 1, IR data of gaseous and liquid methanol, as well as the results obtained after chemisorption of methanol on Fe<sub>2</sub>O<sub>3</sub> [1], TiO<sub>2</sub> and Fe–Ti–O, are reported.

The region around 1000–1100 cm<sup>−1</sup> (Fig. 5a) shows several contributions centred at 1051

cm<sup>−1</sup> (broad peak with a shoulder around 1060 cm<sup>−1</sup>), 1034 cm<sup>−1</sup> and a broad band between 1010 and 1025 cm<sup>−1</sup>. These peaks suggest the presence of gas methanol (1010–1020, 1034 and 1051 cm<sup>−1</sup>), molecularly chemisorbed methanol (1020–1025 cm<sup>−1</sup>) and traces of methoxide (shoulder at 1060 cm<sup>−1</sup>). The broad band around 3300 cm<sup>−1</sup> (Fig. 5b) is probably due to the molecularly chemisorbed methanol, as suggested by its decrease trend, which is very similar to the decrease trend of the peak at 1020–1025 cm<sup>−1</sup> (Fig. 6a). At temperatures higher than 350–370 K, the contributions due to the molecularly chemisorbed alcohol (i.e., 3300 and 1022 cm<sup>−1</sup>) are completely removed, confirming the weakness of the interaction between methanol and surface.

The C–H stretching region (Fig. 5b) shows two main structures centred around 2835 and 2940–2950 cm<sup>−1</sup>. A careful observation reveals the presence of several contributions (2823, 2835, 2922, 2945, 2972 and 3005 cm<sup>−1</sup>) compatible with complex situations in which differ-

Table 1

IR data of vapour and liquid methanol; the IR data obtained after chemisorption of methanol on the Fe<sub>2</sub>O<sub>3</sub> are also shown as well as the data concerning the chemisorption of methanol on the mixed oxide and on the TiO<sub>2</sub>

Assignment	Vapour	Liquid <sup>a</sup>	CH <sub>3</sub> OH/Fe <sub>2</sub> O <sub>3</sub> <sup>b</sup>	CH <sub>3</sub> OH/Fe–Ti–O	CH <sub>3</sub> OH/TiO <sub>2</sub>
Str. C–O	R 1060 Q 1034 <sup>a</sup> vs P 1012	1029 vs	1070	1060 (shoulder) 1051 1034 1010–1025	1055 1034 1020 1005
Bend. OH	1346 <sup>a</sup> m 1340 <sup>c</sup>	1420 m br			
Bend. (a) CH <sub>3</sub> a''	1430 <sup>a,c</sup> w	1420			
Bend. (s) CH <sub>3</sub> a'	1455 <sup>a,c</sup> m	1455 m			
Bend. (a) CH <sub>3</sub> a'	1477 <sup>a,c</sup> m	1480 sh			
Str. (s) CH <sub>3</sub>	2869 2845 <sup>a</sup> s 2826 (2844) <sup>c</sup>	2822 s	2822		
Str. (a) CH <sub>3</sub>	2973 <sup>a</sup> s (2977) <sup>c</sup>	2934 vs	2927	2972 2940–2950	2970–2980 2940–2950
Str. OH	3617 3687 <sup>a</sup> m (3682) <sup>c</sup> 3673	3337 vs br		3300 3692	3300 3689

<sup>a</sup>Ref. [37].

<sup>b</sup>Ref. [1].

<sup>c</sup>Ref. [35].

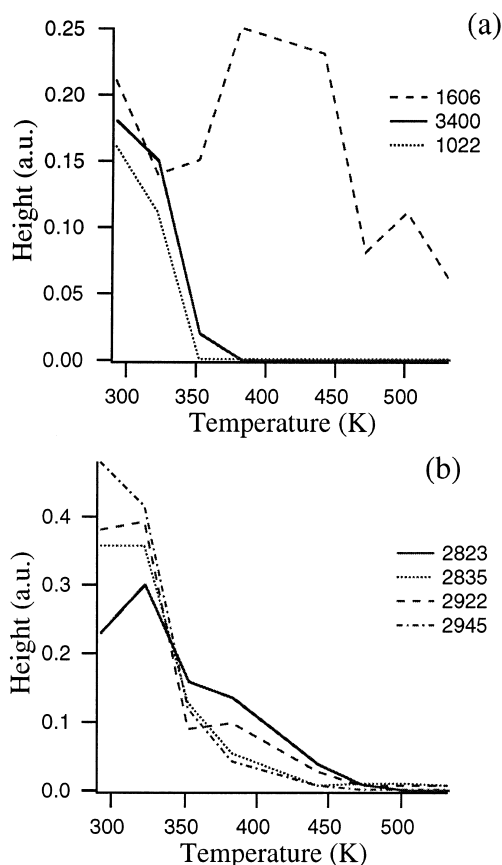


Fig. 6. FTIR results of methanol adsorbed on the Fe-Ti-O mixed oxide at atmospheric pressure and at different temperatures; the height of the main FTIR peaks are shown as a function of the temperature.

ent  $\text{CH}_2$  and  $\text{CH}_3$  groups co-exist. In the C-H stretching regions, all the peaks and shoulders decrease with the temperature and disappear between 400 and 450 K, while, the contributions at 2823 and 2922  $\text{cm}^{-1}$  are still observable at slightly higher temperatures (Fig. 6b) probably being connected with the presence of methoxy groups.

A broad peak can be observed at 3692  $\text{cm}^{-1}$  (Fig. 5b) and may be due to the O-H stretching of the gas alcohol molecules (Table 1) superimposed to the O-H stretching contribution of the Fe-Ti-O powders (3670–3690  $\text{cm}^{-1}$ ). This hypothesis is suggested by the shift of the peak position (toward lower wavenumbers) with the

temperature increase and by its presence at significantly high temperatures (400–500 K).

Small contributions around 1680–1750  $\text{cm}^{-1}$  (Fig. 5c) suggest the presence of C=O bonds coordinated with different a strength to the surface. A peak around 1606  $\text{cm}^{-1}$  with a broad tail at lower wavenumbers can be ambiguously attributed but is usually considered the bending vibration of the water molecules [17,35].<sup>1</sup> It needs to be considered that the intensity of this peak reaches the higher values between 380 and 450 K and then decreases (Fig. 6a).

The FTIR spectra suggest the presence, on the Fe-Ti-O powder surface, of molecularly chemisorbed methanol. Traces of dissociatively chemisorbed methanol (shoulder around 1060  $\text{cm}^{-1}$ , contributions at 2823 and 2922  $\text{cm}^{-1}$ ) cannot be excluded. From these results, it appears that the molecularly chemisorbed methanol is greatly prevalent on the dissociatively chemisorbed. This consideration is confirmed by the spectrum of  $\text{CH}_3\text{OH}$  adsorbed at RT on the Fe-Ti-O powders in rough vacuum conditions.

FTIR spectra obtained after the chemisorption of methanol on the Fe-Ti-O powder in rough vacuum conditions are shown in Fig. 7.

The C-O stretching region does not indicate the presence of methanol molecularly or dissociatively coordinated to the surface because no peaks but a broad band around 980  $\text{cm}^{-1}$  are present in that region. This confirms that methanol is weakly bonded to the surface and can be removed in a rough vacuum.

The complex bands due to the C-H stretching vibrations (Fig. 7a and b) are slightly different with respect to the corresponding ones obtained after chemisorption at atmospheric pressure conditions. The main contributions were centred at 2818 and 2922  $\text{cm}^{-1}$  while less intense appears the contributions at 2931, 2947 and 2972  $\text{cm}^{-1}$ , because the species less tightly bonded to the surface have been eliminated in

<sup>1</sup> See also [6,7,14,15].

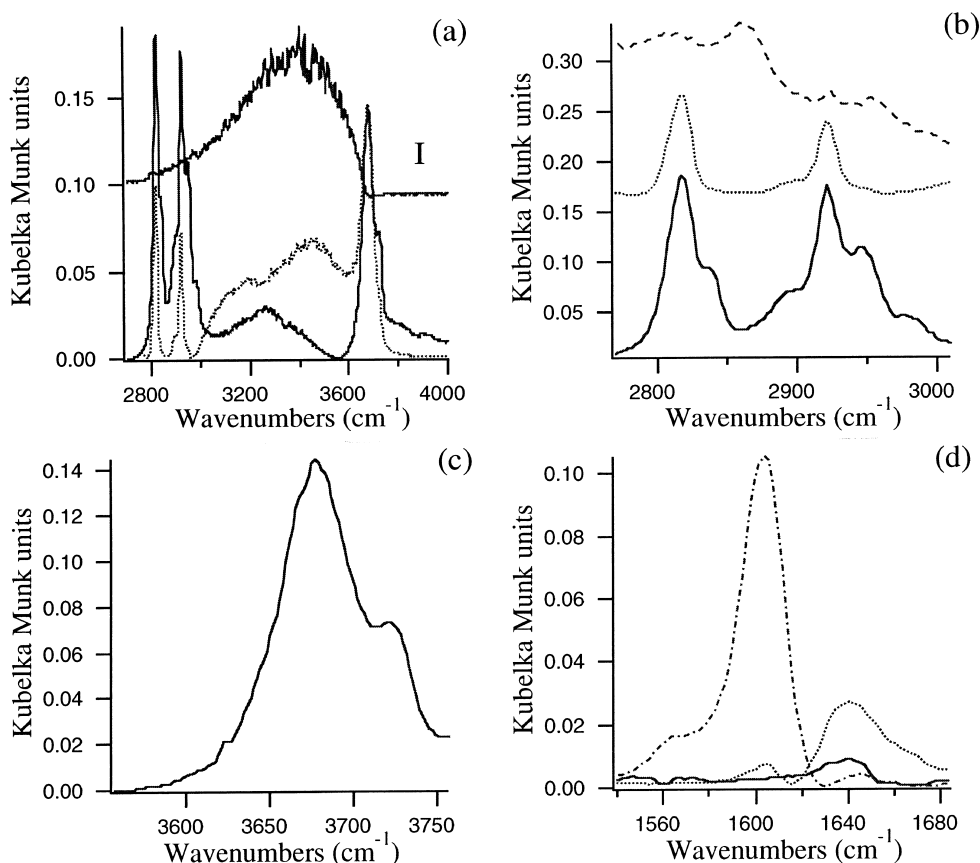


Fig. 7. FTIR spectra of methanol adsorbed on the Fe-Ti-O mixed oxide in rough vacuum conditions and treated at different temperatures (— RT, ..... 473 K, - · - · - 543 K, ---- 673 K): (a) O-H and C-H stretching regions; the spectrum obtained after the exposure of the Fe-Ti-O mixed oxide powders to water (I) is also shown; (b) C-H stretching region; (c) O-H stretching region; (d) region between 1540 and 1680.

vacuum conditions. The spectrum obtained at RT in vacuum conditions is very similar, at this respect, to the spectra obtained at higher temperature in atmospheric pressure conditions. This suggests the presence at low temperatures of reagents and/or products weakly bonded to the surface (which are removed in rough vacuum) and of methoxy groups.

The temperature-increase causes a decrease of all the C-H stretching contributions; upon 473 K new contributions at ca. 2865 and 2954  $\text{cm}^{-1}$  become important (Figs. 8a,b and 7b).

The broad band centred at about 3270–3300  $\text{cm}^{-1}$  (Fig. 7a) appears after heating at 353 K (as in the case of the chemisorption in atmospheric pressure) and a new contribution around

3450  $\text{cm}^{-1}$  appears and grows with the temperature. This last contribution is compatible with the presence of water molecules as confirmed by the comparison with the spectra obtained before the chemisorption (Fig. 4a) and after the chemisorption of water (Fig. 7a).

The O-H stretching region (Fig. 7c) is more defined than in the experiment at atmospheric pressure and shows the presence of two contributions centred at 3722 and 3678  $\text{cm}^{-1}$ . The intensity of these contributions increases slightly as the temperature increase and then decreases; around 570–600 K nothing is anymore visible in this region (Fig. 8b). The position of these peaks is very similar to the values obtained on the  $\text{Fe}_2\text{O}_3$  (3716 and 3670  $\text{cm}^{-1}$ ).

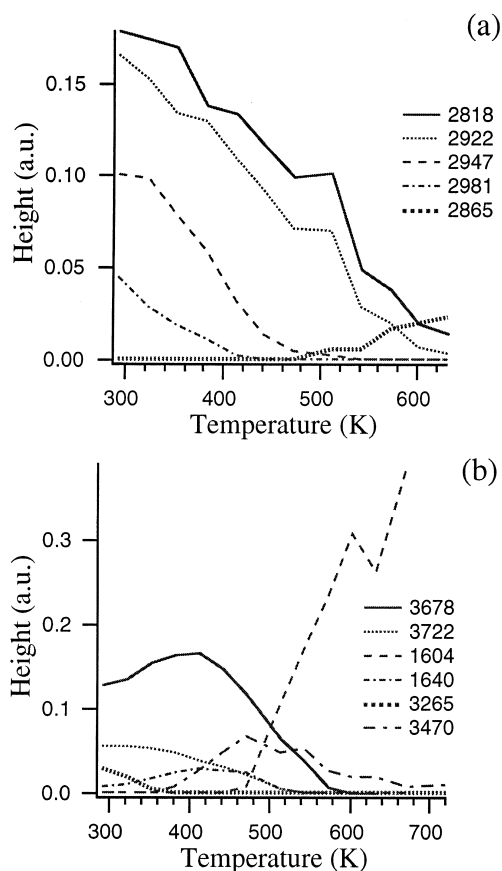


Fig. 8. FTIR results of methanol adsorbed on the Fe-Ti-O mixed oxide in rough vacuum conditions and treated at different temperatures; the height of the main FTIR peaks are shown as a function of the temperature.

A small peak at  $1640\text{ cm}^{-1}$  (Fig. 7d) is present but its attribution is ambiguous: it has to be considered that a contribution at  $1640\text{ cm}^{-1}$  is also present before the chemisorption and can be due to the presence of water. The intensity of the peak centred at  $1640\text{ cm}^{-1}$  increases with temperature and is maximum between 400 and 450 K; around 473 K, a new peak centred at  $1604\text{ cm}^{-1}$  appears and grows with temperature (Figs. 7d and 8b).

The MS spectra of methanol chemisorbed in the HTHP reactor allow to distinguish two main regions of desorption peaks (Fig. 9). The first one (ca. 300–450 K) is related to the desorption of molecularly chemisorbed methanol and of

methane and water. Higher temperature desorption peaks (500–550 K) are due to the decomposition of surface methoxy species, giving rise to water, carbon dioxide and traces of hydrogen. Water desorption suggested by the MS spectra agree with the FTIR results. The presence of nitrogen in the reaction environment does not allow any consideration concerning the CO desorption.

It is interesting to observe the desorption of formaldehyde: the molecularly chemisorbed aldehyde desorbs at low temperature (360–380 K) while more tightly bonded forms of aldehyde desorb at higher temperatures (between ca. 470 and 650 K). In similar experimental conditions, the desorption patterns observed after the chemisorption of methanol on  $\text{Fe}_2\text{O}_3$  [1] is significantly different: no traces of methane or formic aldehyde were evident in that case.

### 3.2.2. Chemisorption of 1-butanol at atmospheric pressure and in HV conditions

In Table 2, IR data of gaseous and liquid butanol are reported.

The FTIR spectrum of the *n*-butanol adsorbed at RT on the Fe-Ti-O powders (Fig. 10) shows two main structures: the broad band around  $3300\text{ cm}^{-1}$  and the CH stretching region (Fig. 10a). In this last region, several peaks are

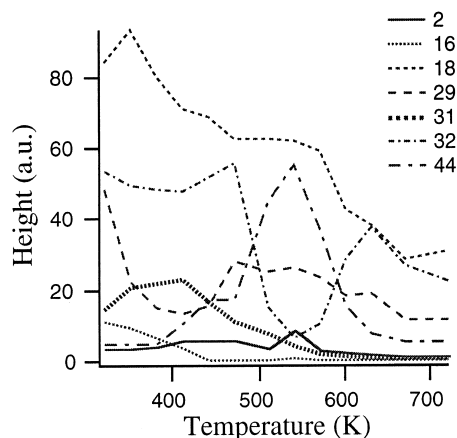


Fig. 9. Desorption patterns obtained from the MS spectra for the Fe-Ti-O mixed oxide exposed to methanol in the HTHP reactor.

Table 2  
IR data of gas and liquid *n*-butanol

	<i>n</i> -Butanol gas <sup>a</sup>	<i>n</i> -Butanol liquid <sup>b</sup>
Str. O–H	3636	3225
Str. (a) CH <sub>3</sub>	2966	
Str. (a) CH <sub>2</sub>	2935	
Str. (a), (s) CH <sub>3</sub> , CH <sub>2</sub>	2880	
Bend. C–H	1460	1461
	1380	1370
Str. C–O	1053	1075

<sup>a</sup>Ref. [38].

<sup>b</sup>Ref. [39].

evident: 2962 cm<sup>-1</sup> (CH<sub>3</sub>-asymmetric stretching), 2937 cm<sup>-1</sup> (CH<sub>2</sub>-asymmetric stretching) and 2870–2880 cm<sup>-1</sup> (CH<sub>3</sub>-symmetric stretching). All these terms are probably due to the presence of butanol on the Fe–Ti–O surface as well as the small bands at 1465 cm<sup>-1</sup> (CH<sub>3</sub> asymmetric bending), 1380 cm<sup>-1</sup> (CH<sub>3</sub> symmetric bending), 1072 cm<sup>-1</sup>.

It is interesting to observe the spectra evolution with the exposure time (Fig. 11); in the O–H stretching region, for example, the peak at 3697 cm<sup>-1</sup> splits into two components centred around 3718 and 3675 cm<sup>-1</sup> (Fig. 11a). It has to be noted that similar positions have been observed in the case of the exposure to methanol.

A small peak at 1640 cm<sup>-1</sup> (Fig. 10c) is evident after the chemisorption at RT and could agree with the presence of the bending vibrations of the water molecules. The intensity of this peak decreases with the exposure time while the contributions in the C–H stretching region, as well as the two bands at 1468 and 1380 cm<sup>-1</sup>, increase (Fig. 11b and c).

All these results suggest that the interaction between the alcohol molecules and the surface is mainly molecular and that the alcohol dissociation is a slow process.

The FTIR data obtained at increasing temperatures are shown in Figs. 10 and 12.

The temperature increment causes the intensity decreases of all the C–H stretching region bands (Figs. 10a and 12). The broad band around 3280 cm<sup>-1</sup> decreases with the temperature disappearing around 350 K (Fig. 12) as in the case

of the chemisorption of methanol at atmospheric pressure. The intensity of the O–H stretching

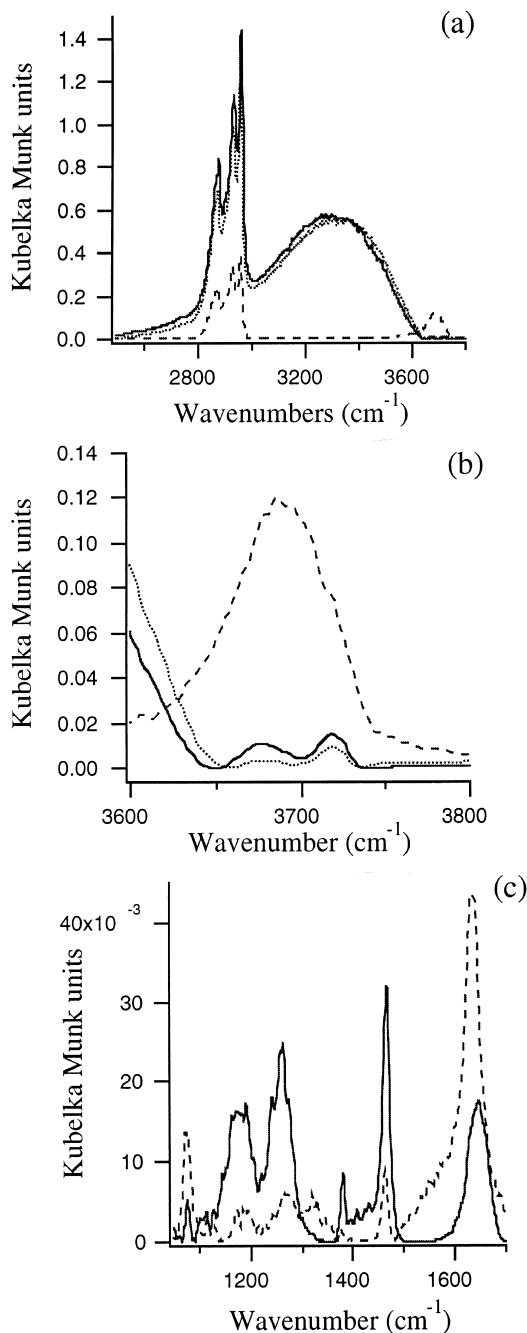


Fig. 10. FTIR spectra of 1-butanol adsorbed on the Fe–Ti–O mixed oxide at atmospheric pressure at different temperatures (— RT, ..... 323 K, - - - 383 K): (a) O–H and C–H stretching regions; (b) O–H stretching region; (c) region between 1050 and 1700 cm<sup>-1</sup>.

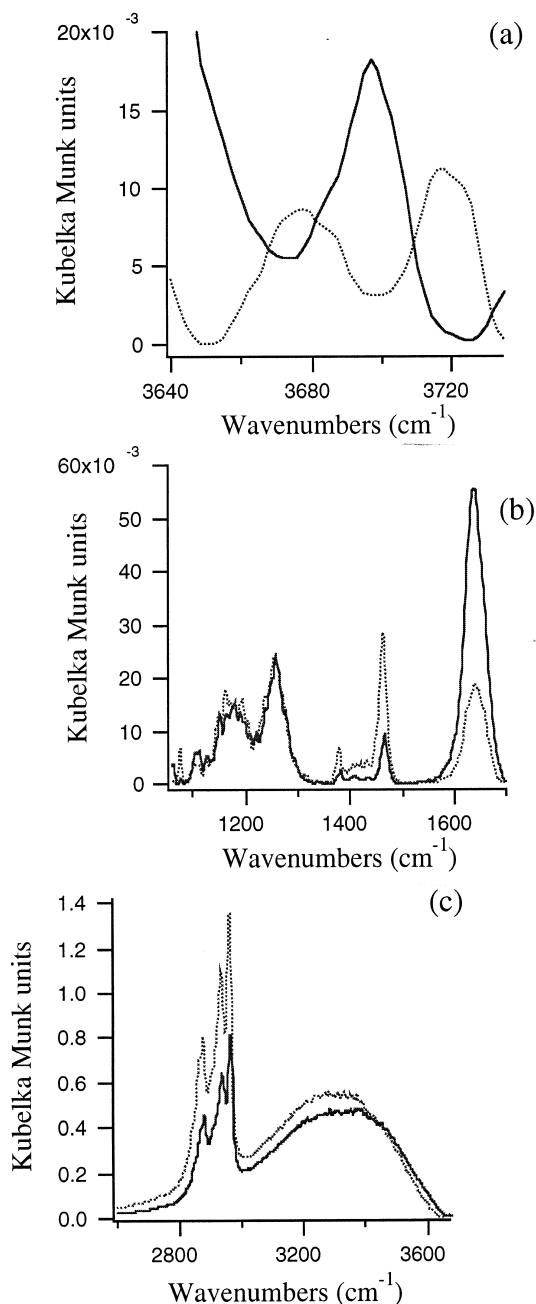


Fig. 11. FTIR spectra of 1-butanol adsorbed (at RT) on the Fe–Ti–O mixed oxide at atmospheric pressure with increasing exposure times (— as exposed, ..... after 10 min of exposure): (a) O–H stretching region; (b) region between 1050 and 1700  $\text{cm}^{-1}$ ; (c) O–H and C–H stretching regions.

region ( $3718$  and  $3675\text{ cm}^{-1}$ ) peaks begins to decrease around  $380$  and  $400\text{ K}$  disappearing completely around  $500$ – $520\text{ K}$ .

The band at  $1640\text{ cm}^{-1}$  slightly grows with the temperature reaching a maximum between  $380$  and  $420\text{ K}$  and then decreases disappearing around  $470\text{ K}$  (Fig. 12). The intensity of the small peaks around  $1261$  and  $1180\text{ cm}^{-1}$  increases between RT and  $323\text{ K}$  and then decreases.

### 3.2.3. Chemisorption of methanol in HV conditions

The broad C 1s peak obtained for the system Fe–Ti–O after chemisorption is centred around  $285.0$ – $285.5\text{ eV}$  (Fig. 13); the fitting procedure shows the presence of two contributions at least, centred at  $285$  and  $286.4$ – $286.6\text{ eV}$ . These contributions can be due to the presence of hydrocarbons (contamination or decomposition products) and of methoxy groups.

The Fe  $2p_{3/2}$ , O 1s and Ti  $2p_{3/2}$  peaks positions (centred around  $710.9$ – $711.4$ ,  $530.0$ – $530.5$  and  $458.3$ – $458.7\text{ eV}$ , respectively) do not change after the chemisorption (Fig. 4). After the reaction, the atomic ratios change slightly: Fe/Ti is  $2.7$  ( $2.4$  before the reaction) while O/(Fe + Ti) becomes  $1.8$  ( $1.9$  before the reaction). XPS data show that after the reaction the surface become slightly oxygen deficient and the Fe/Ti atomic ratio changes slightly.

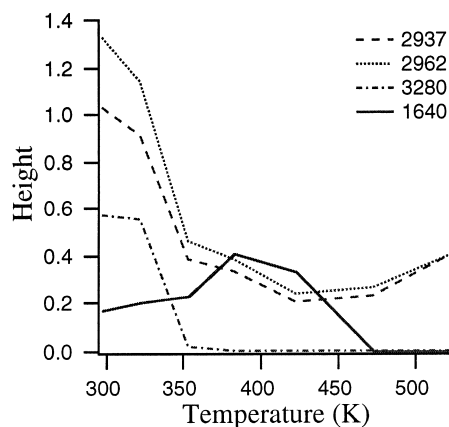


Fig. 12. FTIR results of 1-butanol adsorbed on the Fe–Ti–O mixed oxide at atmospheric pressure and at different temperatures; the height of the main FTIR peaks is shown as a function of the temperature.

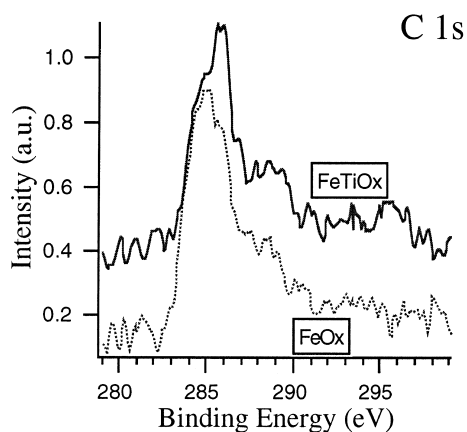


Fig. 13. C 1s spectra obtained after chemisorption of methanol on the (a) Fe-Ti-O catalyst; (b) Fe<sub>2</sub>O<sub>3</sub> [1].

MS data obtained chemisorbing methanol are shown in Fig. 14a and b.

Molecularly chemisorbed methanol desorbs at temperatures lower than 370–400 K while methoxy groups desorb between 400 and 500 K.

It has to be considered that the parent alcohol desorption is not accompanied by water desorption (see the MS data obtained in the HTHP reactor). The main desorbing masses in the investigated temperature range are  $m/e = 15, 16, 18, 28, 29, 30$  and 44 amu. At temperatures between ca. 400 and 500 K (i.e., in coincidence with the methoxy groups desorption), the  $m/e = 15$  amu is prevalent while at higher temperatures the presence of the  $m/e = 16, 18$  and 44 amu becomes evident. The intensity ratios between some peaks may be significant: the ratio 30/29 is always around 1 while the ratio 30/28 is around 0.4–0.5 at low temperatures (between 400 and 520 K) and around 1.3 at higher temperatures. Looking at these data and comparing the intensity ratios with the values expected for hydrocarbons and formaldehyde [25], it can be suggested that, between ca. 400 and 500 K, methoxy groups desorb and decompose giving rise to CH<sub>3</sub> hydrocarbon fragments which can originate C<sub>2</sub>H<sub>6</sub>. At temperatures higher than 500–550 K, methanol decomposes to CH<sub>4</sub>, H<sub>2</sub>O and also gives rise to the formation of CO<sub>2</sub> and

formaldehyde. When a methanol + oxygen mixture is chemisorbed (Fig. 14c), the  $m/e = 15$  amu almost disappears while the other masses

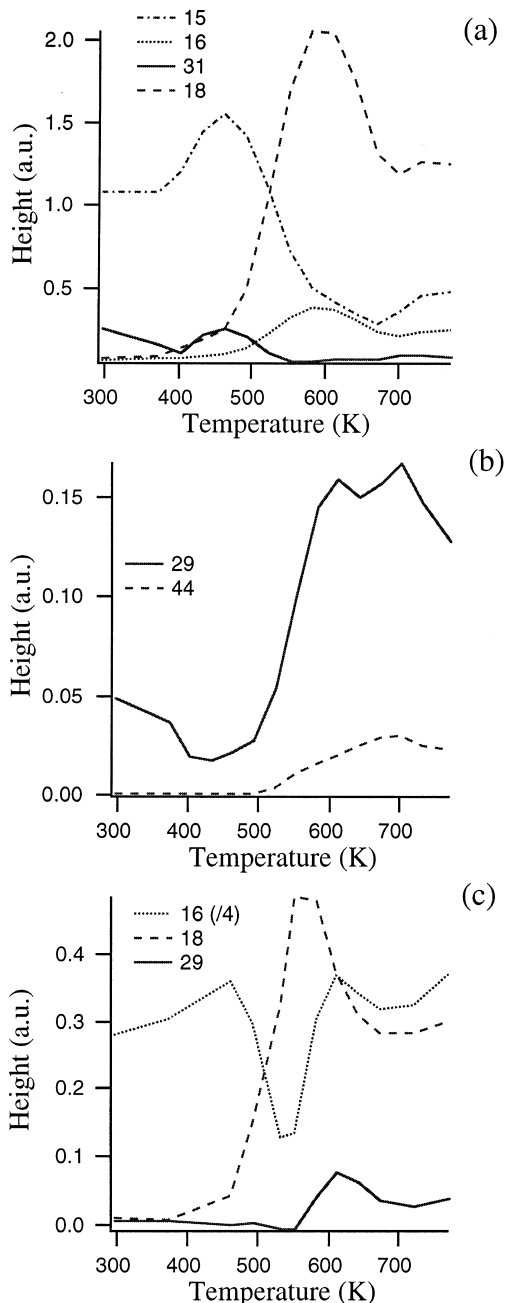


Fig. 14. Desorption patterns obtained (under HV conditions) by the MS spectrum for (a), (b) Fe-Ti-O/methanol; (c) Fe-Ti-O/(methanol + oxygen).



are still present. The masses  $m/e = 29$  and  $30$  amu are almost completely missing at temperatures lower than  $500\text{--}550\text{ K}$ ; at higher temperatures, the intensity of these masses grows and the  $m/e = 29/30$  ratio corresponds to the expected one for formaldehyde ( $= 0.6$ ). All these data suggest that, when oxygen is present, methanol gives rise to the formation of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  and, at temperatures higher than  $550\text{--}600\text{ K}$ , to  $\text{CO}_2$  and formaldehyde; moreover, the fragmentation of the alcohol seems to be poorly relevant.

The MS results obtained in the HV experiment are similar to those observed in the HTHP experiment but, in the absence of oxygen, the methanol fragmentation reaction is important.

### 3.2.4. Chemisorption of higher alcohols in HV conditions

The MS data concerning the desorption results obtained from chemisorbing ethanol are shown in Fig. 15a and b.

Molecularly chemisorbed ethanol desorbs at temperatures lower than ca.  $400\text{ K}$  while ethoxy groups are also present at higher temperatures. At temperatures lower than  $500\text{ K}$ , other masses are present:  $m/e = 28$  and  $29$  amu. This result suggests that the alcohol desorption is accompanied by a fragmentation/decomposition reaction giving rise to hydrocarbons. Traces of carbon monoxide cannot be excluded. At temperatures higher than  $500\text{ K}$ , the intensity of several masses with  $m/e = 16, 18, 28, 29$  and  $44$  amu increases; the masses  $m/e = 16$  and  $18$  amu seem to be correlated and may derive from the decomposition of the alcohol. Also, the masses  $m/e = 29$  and  $44$  amu seem to be correlated and suggest the presence of acetaldehyde. The  $29/44$  ratio ranges around  $0.6$  while the expected value for acetaldehyde is around  $0.8$ ; this may be compatible with the alcohol fragmentation. The presence of oxygen in the reaction mixture does not alter the behaviour of the masses:  $m/e = 16$  and  $18$  amu while the masses  $m/e = 29$  and  $44$  amu decrease. Oxygen seems

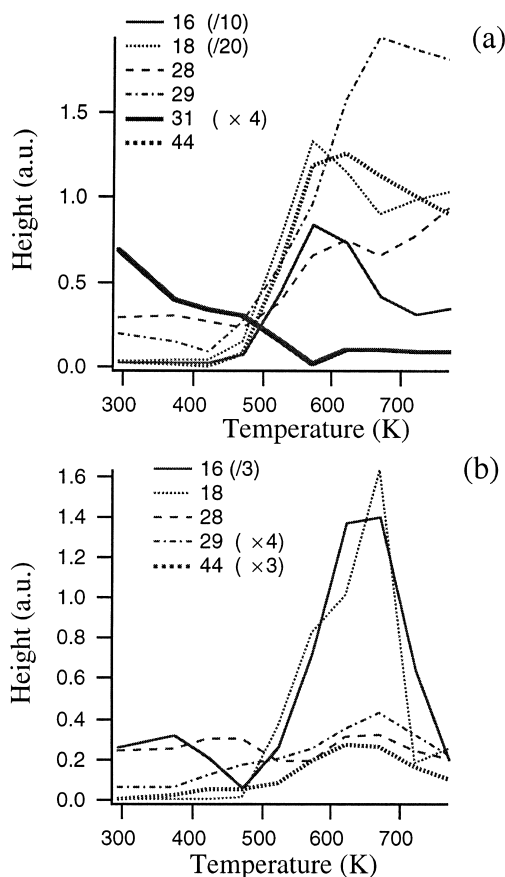


Fig. 15. Desorption patterns obtained (under HV conditions) by the MS spectrum for (a) Fe-Ti-O/ethanol; (b) Fe-Ti-O/(ethanol + oxygen).

to be unfavourable for the fragmentation reaction and for the formation of acetaldehyde.

The MS data concerning the desorption results obtained chemisorbing 1-propanol are shown in Fig. 16a and b.

At temperatures lower than  $400\text{ K}$ , the following masses are present:  $m/e = 16, 18, 28$  amu and traces of the masses  $m/e = 15$  and  $29$  amu suggesting that the alcohol desorption is accompanied by its decomposition and by the formation of methane and water. The  $m/e = 28$  amu is compatible with the presence of  $\text{CO}$  as well as of hydrocarbons. Several masses are present between ca.  $500\text{--}520$  and  $650\text{--}670\text{ K}$ :  $m/e = 2, 16, 18, 25, 26, 27, 28, 29, 30, 39$  and  $44$  amu. These masses suggest the desorption of

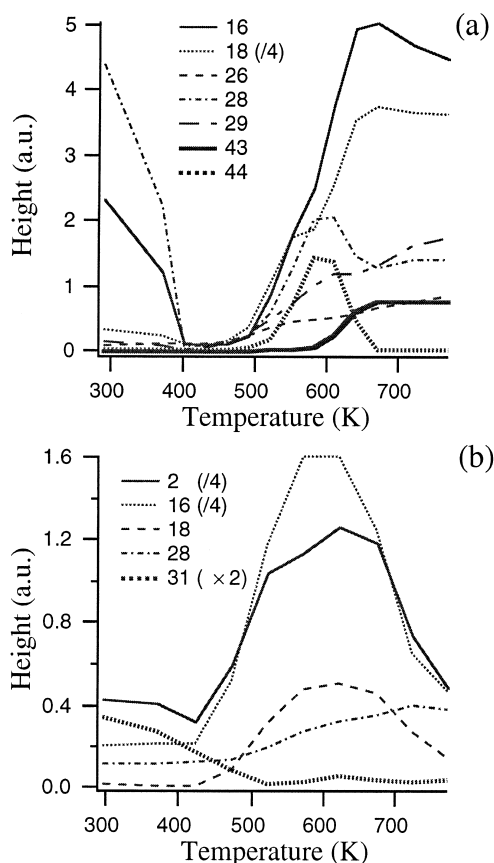


Fig. 16. Desorption patterns obtained (under HV conditions) by the MS spectrum for (a) Fe-Ti-O/1-propanol; (b) Fe-Ti-O/(1-propanol + oxygen).

hydrocarbons and the fragmentation reaction of the *n*-propanol. At temperatures higher than ca. 650 K, a new mass becomes relevant at  $m/e = 43$  amu; this may suggest the presence of the aldehyde. When oxygen is present in the reaction mixture (Fig. 16b), the prevalent reaction seems to be the formation of methane, hydrogen, water and carbon monoxide.

### 3.3. $\text{TiO}_2$

#### 3.3.1. Chemisorption of methanol at atmospheric pressure and in HV conditions

The FTIR spectra of the  $\text{CH}_3\text{OH}$  adsorbed on the  $\text{TiO}_2$  powders at RT, 323, 383 and 413 K,

are shown in Fig. 17. In the region between 960 and  $1090\text{ cm}^{-1}$  (Fig. 17a), several contributions are evident around 1005, 1020, 1034 and  $1055\text{ cm}^{-1}$  suggesting the presence of gas phase methanol (contributions around 1005, 1034 and  $1055\text{ cm}^{-1}$ ) and of molecularly chemisorbed methanol ( $1020\text{ cm}^{-1}$ ). A peak centred at about  $1062\text{ cm}^{-1}$  is compatible with the presence of methoxy groups.

The interaction between methanol and the catalyst surface is weak, as confirmed by the almost complete disappearance of these peaks after heating at temperatures higher than 323 K. At 323 K, the intensity increase of a peak around  $1055\text{ cm}^{-1}$  (with the shoulder around  $1062\text{ cm}^{-1}$ ) is evident. Further temperature increments cause the complete disappearance of all the contribution between 950 and  $1100\text{ cm}^{-1}$ . This result can suggest that the temperature causes a slight increase of the alcohol dissociation; further heating causes the complete desorption of the molecularly chemisorbed methanol.

The region between 2700 and  $3100\text{ cm}^{-1}$  (Fig. 17b) shows two main peaks centred at about 2830 and  $2950\text{ cm}^{-1}$ . A careful observation of the peaks shape allows to discern several contributions 3006, 2980–2970, 2940–2950, 2922, 2866,  $2831\text{ cm}^{-1}$  (with a shoulder around  $2841\text{ cm}^{-1}$ ) suggesting a complex situation in which different  $\text{CH}_3$  and  $\text{CH}_2$  groups are present. The temperature increment causes the decrease of the peaks in the C–H stretching region and at temperatures higher than 323 K only the contributions at 2831, 2922 (probably connected to the presence of methoxy groups) and  $2950\text{ cm}^{-1}$  are still present.

The region between 3100 and  $3800\text{ cm}^{-1}$  (Fig. 17c) is characterised by the presence of a broad band around  $3300\text{ cm}^{-1}$  corresponding to the presence of molecularly chemisorbed methanol. A very intense peak is centred around  $3689\text{ cm}^{-1}$  and is attributed to the gaseous methanol. This peak shows an asymmetry at the higher wavenumber values while a small contribution is visible at  $3674\text{ cm}^{-1}$ . This results suggest the formation of OH groups. The O–H

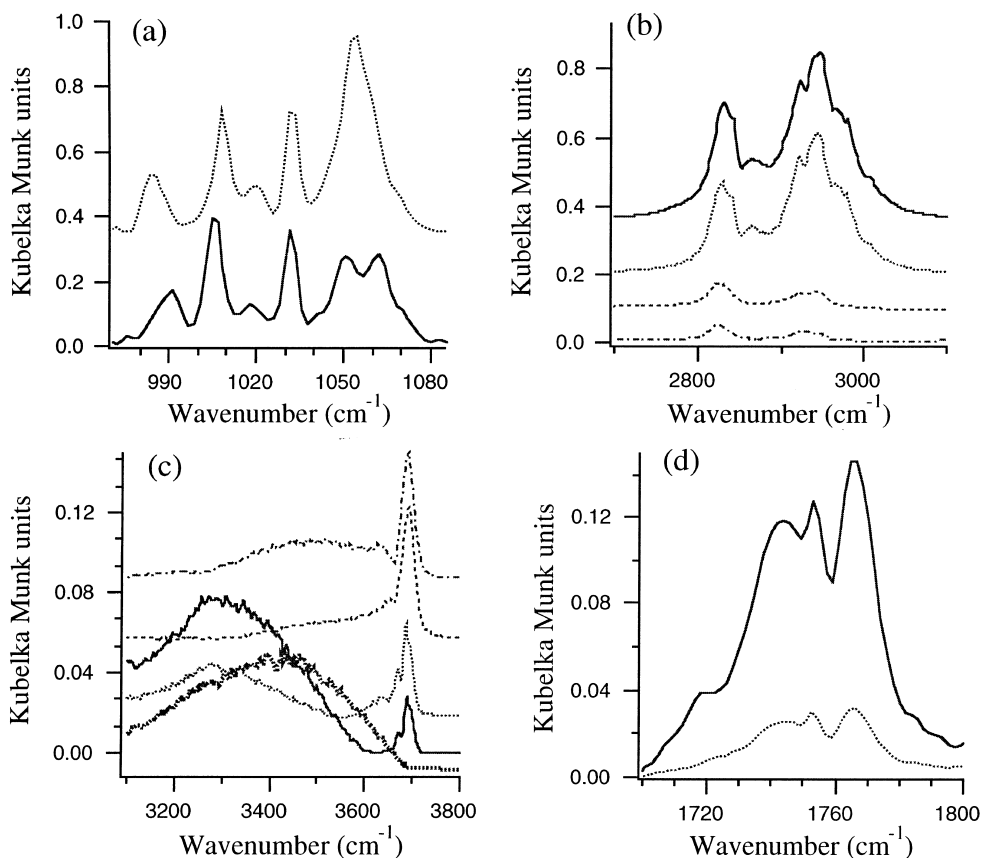


Fig. 17. FTIR spectra of methanol adsorbed on the  $\text{TiO}_2$  at atmospheric pressure and at different temperatures (— RT, ..... 323 K, --- 383 K, - · - · - 413 K): (a) C–O stretchings region; (b) C–H stretching region; (c) O–H stretching region; the spectrum obtained after the chemisorption of water is also shown (|||||||); (d) C=O stretching region.

stretching contribution due to the alcohol molecules disappears upon 323 K while becomes important the peak at  $3695\text{ cm}^{-1}$  (a similar position has been observed in the O–H stretching region of the as calcined  $\text{TiO}_2$  powder) with two shoulders around  $3650$  and  $3674\text{ cm}^{-1}$ .

The broad band at  $3300\text{ cm}^{-1}$  due to the molecularly chemisorbed alcohol also decreases with the temperature and disappears upon 323 K while a new one centred at ca.  $3450\text{--}3500\text{ cm}^{-1}$  appears around  $350\text{--}380\text{ K}$  and grows with the temperature (Fig. 18). This last broad band can be due to the presence of water molecules and of H-bonded OH groups. The attribution of the band around  $3450\text{ cm}^{-1}$  is

confirmed by the spectra obtained before the chemisorption (Fig. 4b) and after the chemisorption of water on the  $\text{TiO}_2$  powder (showing a broad band at ca.  $3430\text{ cm}^{-1}$ ). The broad band around  $3500\text{ cm}^{-1}$  is due to the O–H stretching vibrations. Further temperature increases cause the shift and the widening of this broad band toward lower wavenumbers.

Three small bands at  $1765$ ,  $1753$  and  $1743\text{ cm}^{-1}$  (Fig. 17d) suggest the presence of formic acid molecules (Table 3) weakly bound to the oxide with different strength; these traces of formic acid disappear at temperatures higher than 323 K (Fig. 18). At this temperature, a new peak at  $1640\text{ cm}^{-1}$  is present and disappears around  $380\text{--}420\text{ K}$ .

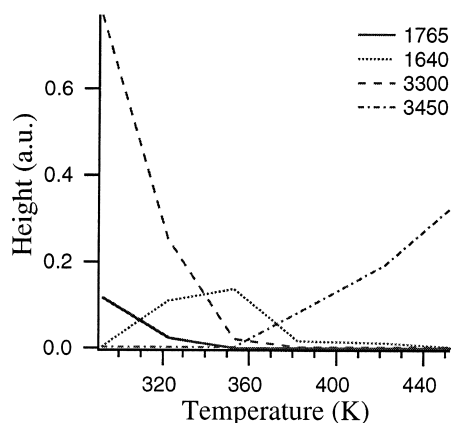


Fig. 18. FTIR results of methanol adsorbed on the  $\text{TiO}_2$  at atmospheric pressure and at different temperatures; the height of the main FTIR peaks is shown as a function of the temperature.

Traces of CO ( $2053$  and  $2073\text{ cm}^{-1}$ ) are present at RT and at  $323\text{ K}$  while  $\text{CO}_2$  ( $2339$ ,  $2357$  and  $2366\text{ cm}^{-1}$ ) has been observed between  $443$  and  $483\text{ K}$ .

The XPS spectra obtained before and after exposing the  $\text{TiO}_2$  surface to methanol in HV conditions are shown in Fig. 2. As it can be seen, the Ti  $2p$  and O  $1s$  peaks position and shape, as well as the O/Ti atomic ratio, do not change after the chemisorption; this suggests that the chemisorption/desorption reactions do not modify the  $\text{TiO}_2$  surface.

The MS data obtained for the chemisorption of methanol on the  $\text{TiO}_2$  powders in HV are reported in Fig. 19. From the figure, it can be seen that molecularly chemisorbed methanol desorbs at temperatures lower than ca.  $380\text{--}400\text{ K}$  while dissociatively chemisorbed methanol desorbs around  $400\text{--}470\text{ K}$ .

Kim et al. [3] and Kim and Barteau [4] found that the TPD spectra of alcohols chemisorbed at RT on the polycrystalline titania exhibited two principal groups of desorption peaks. The first group appeared near  $390\text{ K}$  and was identified as the parent alcohol accompanied by water. The other group appeared at higher temperatures and was considered to result from the decomposition of chemisorbed alcohol species. In the case of methanol, the major decomposition products were formaldehyde, dimethyl ether, methane, carbon monoxide and water. Minor products were methanol and hydrogen.

In the present case, the presence of water with the parent alcohol was not observed. At higher temperatures ( $500\text{--}700\text{ K}$ ), the alcohol decomposes giving rise to hydrocarbons (methane), formaldehyde and water. Hydrocarbon fragments form around  $450\text{--}500\text{ K}$  while  $\text{H}_2\text{O}$  desorbs around  $600\text{--}650\text{ K}$  as well as the  $m/e = 16$ ,  $29$  and  $30$  amu (corresponding to

Table 3

IR data ( $\text{cm}^{-1}$ ) of formic aldehyde, formic acid; the data obtained after exposure of the  $\text{Fe}_2\text{O}_3$  to  $\text{H}_2\text{CO}$  and  $\text{HCOOH}$  (RT) are also shown

	$\text{H}_2\text{CO}$ gas <sup>a,b,c</sup>	$\text{HCOOH}$ <sup>a,d</sup>	$(\text{HCOOH})_2^d$	$\text{H}_2\text{CO}/\text{Fe}_2\text{O}_3^e$	$\text{HCOOH}/\text{Fe}_2\text{O}_3^2$
Str. O–H		3570	3110		3101 3010
Str. (a) $\text{CH}_2$	2874 (vs)			2870	
Str. (s) $\text{CH}_2$	2780 (s)			2770	
Str. CH		2940 (s)	2957 (vs)		2939
Str. C=O	1743 (vs)	1770 (vs)	1754 (vs)	1620	1735 1745
Bend. OCO					
Bend. $\text{CH}_2$	1503 (s)				
Bend. CH		1387	1365 (s)		
Bend. OH		1229	1450 (vw)		1216
Str. C–O					

<sup>a</sup>Ref. [35].

<sup>b</sup>Ref. [40].

<sup>c</sup>Ref. [41].

<sup>d</sup>Ref. [42].

<sup>e</sup>Ref. [43].

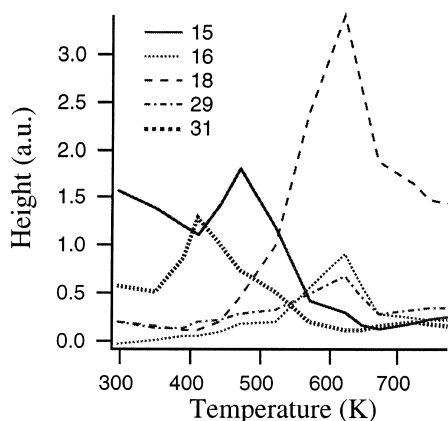


Fig. 19. Desorption patterns obtained (under HV conditions) by the MS spectrum for  $\text{TiO}_2$ /methanol.

methane and formaldehyde). Hydrogen shows two desorption peaks centred at 473 and 623 K. Traces of CO are revealed around 350 and 623 K. The absence of the peaks at  $m/e = 28$ , 45 and 46 amu allows to exclude a significant formation of dimethyl ether.

#### 4. Discussion

One of the first step to consider when dealing with heterogeneous catalysis and surface reactivity is the interaction between the reagents and the catalyst surface. In the case of the interaction between alcohols and oxide surface, the mechanism of chemisorption on an oxide surface strongly depends on the degree of hydroxylation of the surface. On an “ideal” dehydroxylated surface, the mechanism can be dissociative to produce hydroxyl and alkoxy groups or molecular via the interaction with the Lewis acid or basic sites. Three further types of chemisorption modes can be possible on an hydroxylated surface (on which Brönsted acid sites and chemisorbed water molecules are present): replacement of molecular water present on the surface, esterification with acid surface hydroxyls and reversible adsorption on the surface hydroxyls [36].

Fig. 20 shows the spectra of Fe–Ti–O obtained before and after methanol and/or water

chemisorption at RT. The observation of these spectra suggests that the alcohol chemisorption changes the distribution of the OH groups with stretching vibrations at wavenumbers higher than  $3600\text{ cm}^{-1}$ . The chemisorption of water, on the contrary, affects mainly the OH groups with stretching vibrations at wavenumbers lower than  $3600\text{ cm}^{-1}$ . When the methanol chemisorption follows the exposure to the water vapours, the IR spectrum is very similar to that obtained after the chemisorption of water but a contribution around  $3690\text{ cm}^{-1}$  disappears. In any case, the exposure to water influences the active sites for the alcohol interaction preventing the successive chemisorption of methanol (Fig. 20b).

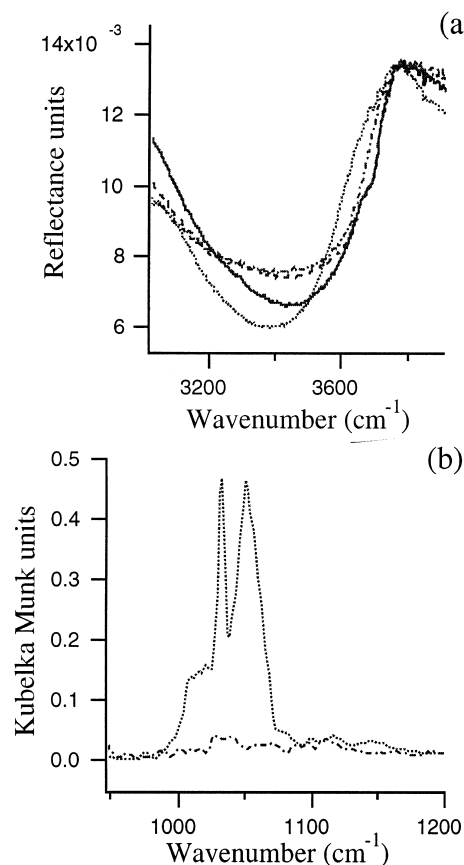


Fig. 20. FTIR of the Fe–Ti–O mixed oxide. (a) Reflectance spectra obtained before the exposure (—), after exposure to methanol (.....), after exposure to water (---) and after the exposure to water and successively to methanol (- · - · - · -).

As can be seen from the obtained results, the reactivity of the  $\text{Fe}_2\text{O}_3$  is changed by the titanium addition. In particular, the mixed oxide does not dissociate methanol (probably because of the different distribution and strength of the Brönsted acid sites) and does not induce the formation of formic acid or formate (suggesting a lower oxidising power). The mixed oxides can then offer interesting opportunities in catalysis; the possibility to control the acid/basic sites as well as the red/ox sites may allow the planning of catalysts characterised by selectivity properties interesting in the applied field. For this reason, in our laboratory, experimental work concerning Fe–Ti–O mixed oxides is in course aiming to the understanding of the surface sites formation mechanisms and control as a function of the different composition and/or preparation procedure.

## 5. Conclusions

In this paper, we studied the interaction between simple alcohols and a Fe–Ti mixed oxide comparing these results with those obtained on  $\text{TiO}_2$  powders. The reactivity of  $\text{Fe}_2\text{O}_3$  was investigated in previous works [1,2].

(1) The reactivity of this mixed oxide is very different with respect to the reactivity of the pure  $\text{Fe}_2\text{O}_3$ ; in this last case, methanol strongly interacts with the surface chemisorbing dissociatively. Iron oxide easily gives up an oxygen atom to the methoxy groups allowing the formation of formate. The Fe–Ti–O mixed oxide seems to be less reactive with respect to the iron oxide: the interaction between the alcohol and the surface is mainly molecular, as in the case of  $\text{TiO}_2$ . The presence of titanium strongly decreases the number/strength of the acid and basic sites. Moreover, oxidising power of the mixed oxide is lower (decrease of the number/strength of the red ox sites).

(2) Molecularly chemisorbed methanol (weakly bonded to the Fe–Ti–O surface) is

greatly prevalent on the dissociatively chemisorbed; molecularly chemisorbed methanol desorbs from the surface around 360–380 K while at higher temperatures (500–550 K) methoxy species decompose to water, hydrogen and carbon oxides.

(3) Molecularly chemisorbed formaldehyde desorbs from the Fe–Ti–O powders exposed to methanol at low temperature (360–380 K) while more tightly bonded forms desorb at higher temperatures (500–650 K).

(4) The interaction between the higher alcohol (1-butanol) molecules and the Fe–Ti–O surface is slow and, essentially, molecular (only traces of alkoxy groups). Chemisorbed butanol desorbs at low temperature (350–400 K).

(5) XPS data show that after the chemisorption of methanol on the Fe–Ti–O mixed oxide in HV conditions, the surface becomes slightly oxygen-deficient; the Ti atomic percentage also decreases. Molecularly chemisorbed methanol desorbs, in HV conditions, at temperatures lower than 370 K, while methoxy groups desorb between 400 and 500 K. Between ca. 400 and 500 K, methoxy groups desorb and decompose giving rise to  $\text{CH}_3$  hydrocarbon fragments which can originate  $\text{C}_2$  hydrocarbons. At temperatures higher than 500–550 K, methanol decomposes to  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and also gives rise to the formation of  $\text{CO}_2$  and formaldehyde. When a methanol + oxygen mixture is chemisorbed, it is evident the desorption of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  and, at higher temperature, to  $\text{CO}_2$ . At temperatures higher than 500 K, the formation of formaldehyde becomes important.

(6) When higher alcohols are chemisorbed on the Fe–Ti–O mixed oxide in HV conditions their desorption (usually at temperatures lower than 400 K) is accompanied by a fragmentation/decomposition reaction giving rise to hydrocarbons, hydrogen and water. Traces of carbon monoxide cannot be excluded. At temperatures higher than 500–600 K, the desorbed masses may derive from the decomposition of the alcohol and from the presence of acetaldehyde.

(7) Methanol chemisorbs mainly molecularly on the  $\text{TiO}_2$  surface; the interaction is weak as confirmed by the almost complete disappearance of these peaks after heating at low temperature (higher than 323 K). The temperature causes a slight increase of the alcohol dissociation and the complete desorption of the molecularly chemisorbed methanol. Traces of formic acid form at RT while around 323 K FTIR spectra suggest the presence of carbonilic compounds tightly bonded to the surface. These species disappear around 380–420 K.

(8) In the HV experiment ( $\text{CH}_3\text{OH}/\text{TiO}_2$ ), molecularly chemisorbed methanol desorbs at temperatures lower than 350–380 K while dissociatively chemisorbed methanol desorbs around 400–450 K. Hydrocarbon fragments form around 450–500 K, while  $\text{H}_2\text{O}$  desorbs around 600–650 K as well as other masses suggesting the presence of aldehyde and hydrocarbons.

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