FTIR study of methanol decomposition on gold catalyst for fuel cells

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Abstract

The interaction of methanol (m), methanol–water (mw) and methanol–water–oxygen (mwo) on Au/TiO$_2$ catalyst has been investigated by in situ infrared spectroscopy (FTIR) and quadrupole mass spectrometry (QMS) at different temperatures. The aim of the work is to elucidate the nature and the abundance of the surface intermediates formed in different experimental conditions and to understand the mechanisms of methanol decomposition, of steam reforming and of combined reforming reactions. FTIR spectra run at room temperature in the different reaction mixtures show that differently coordinated methoxy species, that is on top species adsorbed on oxygen vacancy sites, on top species on uncoordinated Ti^{4+} sites and bridged species on two Ti^{4+} ions, are produced in all the mixtures. Quite strong formaldehyde and formate species adsorbed on gold are produced already at 403 K only in the combined reforming reaction mixture. At 473 K, on top species on uncoordinated Ti^{4+} sites and methoxy species adsorbed on oxygen vacancy sites reduce their intensity and, at the same time, some formate species adsorbed on the support are produced in the steam reforming and combined reforming mixtures. At 523 K, on both methanol and methanol–water reaction mixtures, no more definite surface species are evidenced by FTIR on the catalysts, while in the methanol–water–oxygen mixture some residual methoxy and formate species are still present. Moreover, methanol is no more detected by QMS in the gas phase. A role of oxygen adsorbed on gold particles near oxygen vacancies of the support in the oxidative dehydrogenation of methanol is proposed.
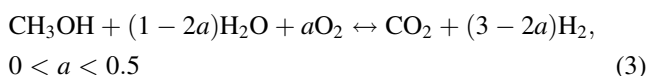© 2003 Elsevier Science B.V. All rights reserved.

Keywords: In situ FTIR and QMS; Gold; Methanol; Steam reforming; Combined reforming

1. Introduction

Fuel cells show many advantages over storage batteries for transportation for on-board electrical power generation: they represent almost "zero emission vehicle" if they are fed directly by H$_2$ or at least a "near zero emission vehicle" if they are fed by conventional fuels which are transformed to H$_2$ via reformer. In this case they are not affected by the limits of electrical vehicles based on storage batteries, as weight, low energy density, etc. [1].

As for automobile applications, hydrogen-rich gas can be produced on-board by methanol decomposition (reaction (1)), by methanol steam reforming (reaction (2)) or by the so-called combined or autothermal reforming where some oxygen is added (reaction (3)):

$$CH_3OH \leftrightarrow 2H_2 + CO \tag{1}$$

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \tag{2}$$

$$CH_3OH + (1 - 2a)H_2O + aO_2 \leftrightarrow CO_2 + (3 - 2a)H_2,$$
$$0 < a < 0.5 \tag{3}$$

The most widely studied catalysts for these reactions are the low temperature catalysts of methanol synthesis, that is Cu/ZnO catalysts and their modifications [2,3]. On these catalysts, in a temperature programmed methanol decomposition study on a partially oxidized sample, it has been shown by mass spectrometry that CO$_2$ and H$_2$ were simultaneously produced at 440 K by the decomposition of a formate species adsorbed on copper sites. At 580 K, CO and H$_2$ were evolved by the decomposition of a formate species on ZnO [4]. However, a full understanding of the reaction mechanisms is not already get. In a steam reforming study of Cu/ZnO/Al$_2$O$_3$ catalyst [3], it has been shown recently that all the above-mentioned reactions must be included in the kinetic analysis in order to explain the complete range of observed product compositions. Moreover, there are evidences that the decomposition reaction occurs on a different type of active site than the other two reactions.

CO is produced in all the reactions not only as a consequence of the direct methanol decomposition (1) at relatively high temperature and high conversions, but also as a by product in reactions (2) and (3) by the occurrence of the reverse water gas shift reaction:

$$CO_2 + 3H_2 \rightarrow CO + H_2O \tag{4}$$

This reaction is usually catalyzed by the same catalysts.

It is well known that the metallic electrocatalysts of the fuel cell anode are poisoned by CO in concentration exceeding few ppm. Hence, present days reforming technologies require some type of CO clean-up before the inlet in the fuel cell. It will be interesting to find a catalyst and/or the feed conditions that allow an efficient methanol decomposition and a reduced level of CO already in the reforming reaction. Alternatively, the obtained gas mixture can be cleaned on an other portion of the same catalyst at lower temperature in order to perform the preferential selective oxidation of CO in presence of hydrogen. Among the best catalysts for this reaction at low temperatures, gold nanodispersed catalysts appear as very active and selective [5]. Keeping in mind the goal of elucidating the mechanisms of the reactions and looking for the abatement of the reaction temperatures and of the CO production, we have undertaken an in situ FTIR and quadrupole mass study of methanol decomposition on Au/TiO_2 catalyst at different temperatures and in different conditions, i.e. in pure methanol, in steam reforming conditions and in combined reforming conditions. The aim of the work is to identify surface and gas phase species, being the intermediates and/or the final products detected in different atmospheres and at increasing temperatures.

2. Experimental

The sample was prepared by the deposition–precipitation method [6]. The gold loading is 3 wt.%. The average gold particle size is 4.1 ± 0.5 nm, as determined by transmission electron microscopy. The sample was calcined at 673 K after the preparation, while, before the experiments, it was preliminary heated up to 673 K in dry oxygen and cooled down in the same atmosphere, then reduced in hydrogen up to 523 K and outgassed for 10 min at the same temperature.

The FTIR spectra have been collected on a Perkin-Elmer 2000 spectrometer equipped with a MCT detector. The sample, as a self-supporting pellet, was introduced in an AABSPEC 2000 cell allowing to run the spectra in situ in controlled atmospheres and temperatures. Different mixtures were put in contact with the catalyst: methanol, that will be indicated as (m), methanol–water (mw) (1:1 ratio) and methanol–water–oxygen (mwo) (1:1:0.2 ratio). The spectra are collected in static conditions, the sample remains 15 min at each temperature, simulating short contact times. Moreover, the spectra have been recorded after one night at the maximum temperature reached. In this way, the equilibrium composition of the gas phase was reached after a long contact time. In all cases, the spectrum of the bare sample at each temperature was subtracted from the absorbance spectra recorded at the same temperature. The cell is connected through a needle valve to a VGQ Thermo ONIX spectrometer equipped with a Thoria filament and a Faraday detector, to obtain the analysis of the gas phase during the reaction. The gas phase composition of the different initial gas mixtures and during the reactions was determined by recording the mass spectrum, using a leak valve set to maintain a 10^{-6} mbar pressure in the detection chamber.

3. Results

3.1. FTIR spectra analysis

FTIR absorbance spectra obtained by interaction with (m), (mw) and (mwo) mixtures on the Au/TiO_2 catalyst at room temperature (RT) (Fig. 1) and by heating in the same mixtures at 403 K (Fig. 2) and at 473 K (Fig. 3) are shown.

At RT, the interaction with the above-mentioned reaction mixtures produces spectra with a similar profile in the
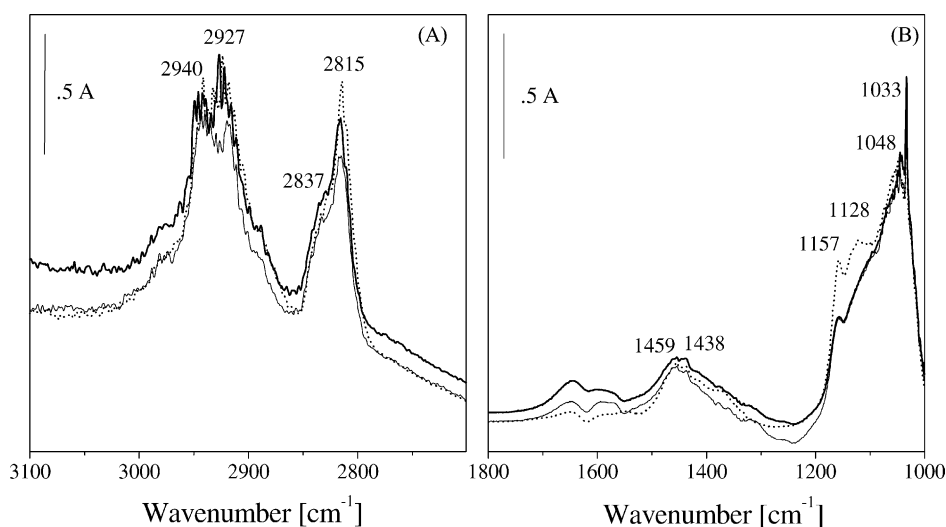

Fig. 1. FTIR absorption spectra obtained by interaction with (m) (dotted curve), (mw) (bold curve) and (mwo) (thin curve) mixtures on the Au/TiO_2 catalyst at RT in the (A) $\nu(CH_3)$ region; and (B) $\nu(OC)$ region.
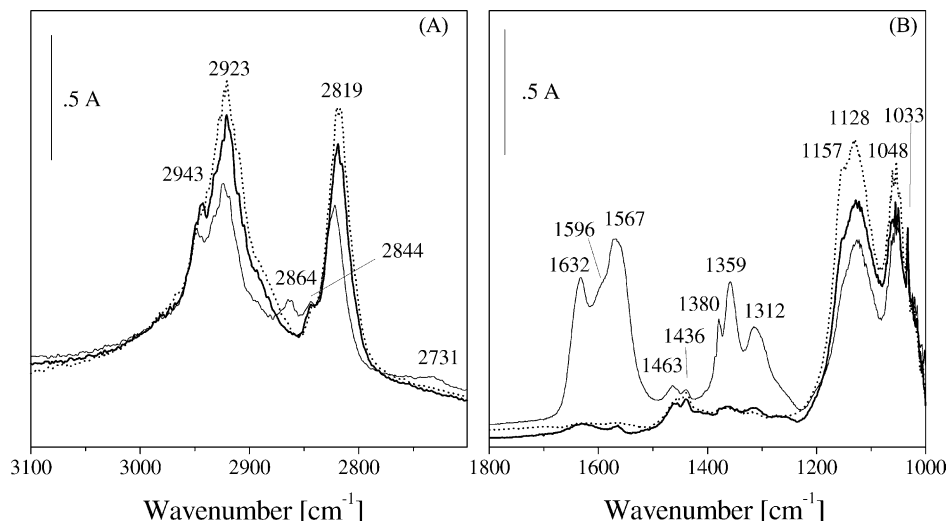
Fig. 2. FTIR absorption spectra obtained by interaction with (m) (dotted curve), (mw) (bold curve) and (mwo) (thin curve) mixtures on Au/TiO$_2$ at 403 K in the (A) $v(CH_3)$ region; and (B) $v(OC)$ region.

range 3100–2700 cm^{-1} (Fig. 1A) and in the range 1800–1200 cm^{-1} (Fig. 1B), while, in the range 1200–1000 cm^{-1}, bands at 1157, 1128 and 1048 cm^{-1} are evident in pure methanol (Fig. 1B).

The $v(CH)$ stretching modes, being the CH$_3$ units not directly bonded to the surface, are less influenced by the nature of the adsorption sites than the $v(OC)$ modes. Therefore, the 1200–1000 cm^{-1} region is more useful than the 3100–2700 cm^{-1} range for the identification of the adsorbed species.

Looking at the literature data concerning methanol adsorption on titania [7] and other oxides [8], the bands at 1157, 1128 and 1048 cm^{-1}, can be assigned to differently coordinated methoxy species adsorbed on the support. We can tentatively propose that the band at 1157 cm^{-1} could be related to on top methoxy species on Ti^{3+} near to an oxygen

vacancy and to metallic gold, the one at 1128 cm^{-1} to on top species on Ti^{4+} sites and the last band at 1048 cm^{-1} to two-fold bridged methoxy species on Ti^{4+} sites (see Table 1).

At 403 K (Fig. 2A), almost identical bands related to the vibrational modes of methoxy species as for (m) (dotted curve) and (mw) (bold curve) mixtures are present in the 3100–2700 cm^{-1} region. The bands related to methoxy species (see Table 1) exhibit a significantly lower intensity and new components, at 2864 and 2731 cm^{-1} are present, when considering the (mwo) mixture (thin curve). The (m) and the (mw) experiments exhibit a quite similar spectrum in the 1800–1000 cm^{-1} region, too, i.e. very weak bands in the 1600–1300 cm^{-1} region and strong bands in the 1150–1050 cm^{-1} range (Fig. 2B, dotted and bold curves, respectively). The low frequency bands with maxima at 1157, 1128 and 1048 cm^{-1} have a reduced intensity in the (mwo)
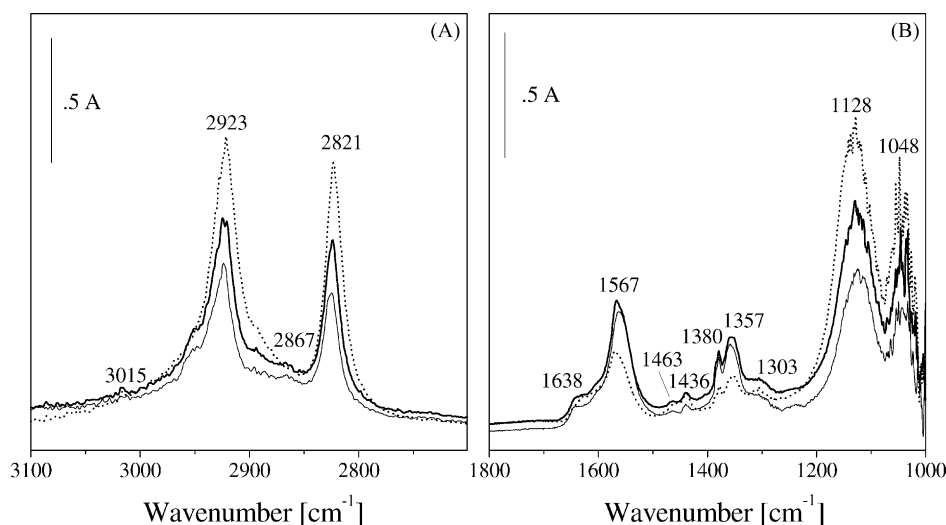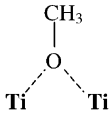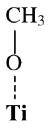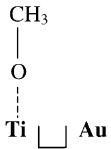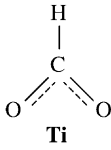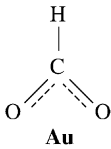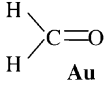

Fig. 3. FTIR absorption spectra obtained by interaction with (m) (dotted curve), (mw) (bold curve) and (mwo) (thin curve) mixtures on Au/TiO$_2$ at 473 K in the (A) $v(CH_3)$ region; and (B) $v(OC)$ region.

Table 1
Assignments of species detected by FTIR spectroscopy in different atmospheres at increasing temperatures

Surface species		Number of modes	Frequencies (cm^{-1})
Methoxy doubly bridged on the support	CH_3—O bridged on Ti⋯Ti	4	2918, 2816, 1459, 1048
Methoxy on top on TiO_2	CH_3—O on Ti	3	2920, 2822, 1128
Methoxy on top on TiO_2 near an oxygen vacancy and near Au	CH_3—O on Ti□Au	4	2923, 2817, 1438, 1157
Formate on TiO_2	H–C(O)(O) on Ti	4	2864, 1567, 1380, 1359
Formate on Au	H–C(O)(O) on Au	3	2950, 1632, 1312
Formaldehyde on Au	H_2C=O on Au	3	2844, 2731, 1596

mixture (Fig. 2B, thin curve). Moreover, new components at 1632, 1596, 1567, 1380, 1359 and 1312 cm^{-1} are produced. The bands at 2864, 1567, 1380 and 1359 cm^{-1}, on the basis of literature data [7], can be assigned to formate species adsorbed on titania. The bands at 2950, 1632 and 1312 cm^{-1} can be related to formate in interaction with gold sites, while the band centered at 1596 cm^{-1}, together with the bands at 2731 and 2844 cm^{-1} can be tentatively assigned to formaldehyde adsorbed on gold (see Table 1). These assignments are made taking in account the low thermal stability of the species, the similarity with bands detected on copper catalysts [9] and some SERS data concerning the electro oxidation of methanol and formic acid on gold electrodes [10].

By heating at 473 K (Fig. 3A and B), the intensity of the bands ascribed to formate and formaldehyde species on gold strongly decrease if we consider the interaction with the (mwo) mixture (thin curve). As for the (mw) mixture (bold curve), the formates on the support grow up and get an intensity almost coincident with those observed in contact with the (mwo) mixture (thin curve) at the same temperature. In the case of the (m) decomposition (dotted curve), the intensity of the bands related to formate species is weaker, about half in respect to the other reaction atmospheres. The intensities of the bands related to methoxy species present in the spectral regions of C–H stretching (3100–2700 cm^{-1}) and of C–O stretching (1200–1000 cm^{-1}) follow the order: decomposition > steam reforming > combined reforming, confirming the correlation between the bands and the assignment already proposed.

By heating at higher temperature (523 K, Fig. 4A and B), almost no adsorbed species are observed in (m) and in (mw) mixture experiments (dotted and bold curves, respectively). In the (mwo) mixture bands related to methoxy and formate species are still present (thin curve).

3.2. Quadrupole mass results

The main changes and differences in the gas phase composition are observed after one night of interaction at 523 K (Fig. 5A–C). Methanol is completely absent in the gas phase in all cases.

Hydrogen and CO, together with significant amounts of methane, CO_2 and traces of formaldehyde are detected after the decomposition of pure methanol (Fig. 5A). Both carbon dioxide and formaldehyde are oxidation products. They are
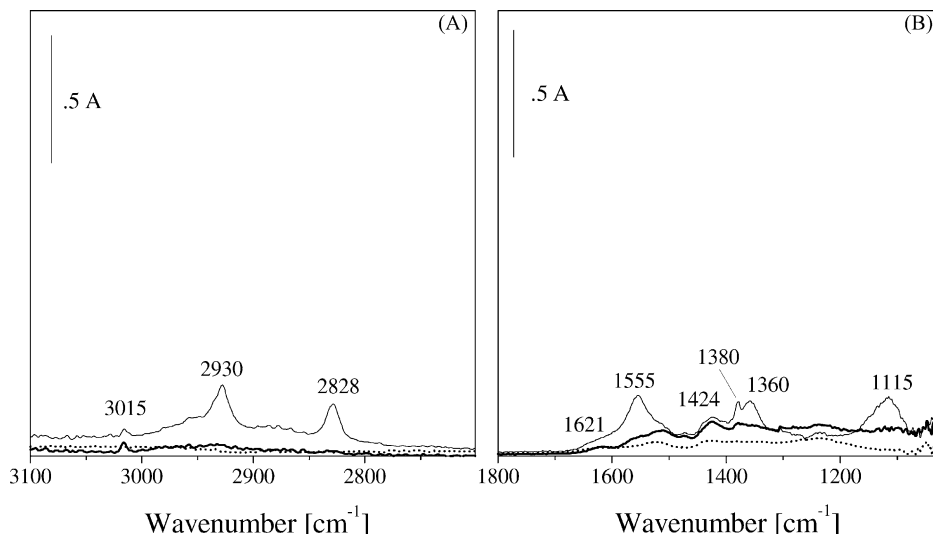
Fig. 4. FTIR absorption spectra obtained by interaction with (m) (dotted curve), (mw) (bold curve) and (mwo) (thin curve) mixtures on Au/TiO$_2$ after one night at 523 K in the (A) v(CH$_3$) region; and (B) v(OC) region.

probably produced by a reductive interaction with the support and by the thermal decomposition of the formate species detected in the FTIR spectra.

Fig. 5. Quadrupole mass spectra collected after one night of interaction with (A) (m); (B) (mw); and (C) (mwo) mixtures at 523 K.

An higher amount of hydrogen is produced during the steam reforming reaction (Fig. 5B). However, in spite to the presence of an excess of water, some CO is still observed. Similar results are observed in presence of oxygen, too (Fig. 5C).
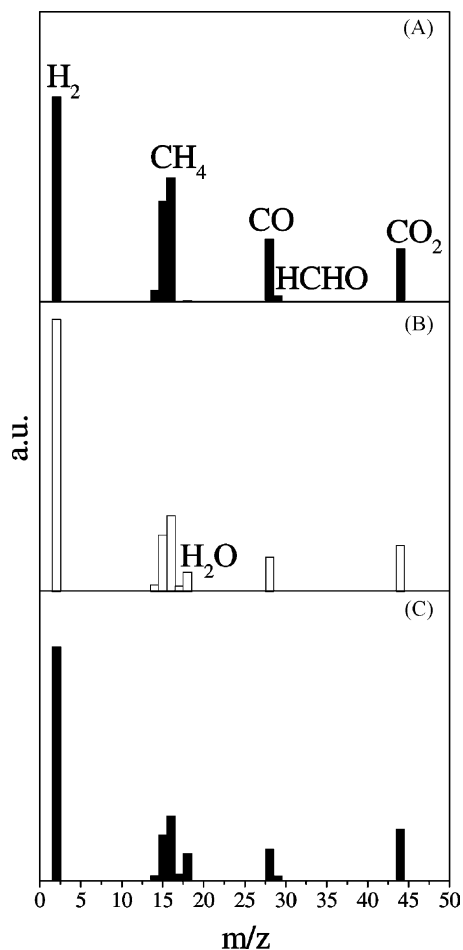
4. Discussion

4.1. Nature of the surface sites involved in the reactions

Different methoxy species (bridged, on top and "modified" on top near an oxygen vacancy) have been evidenced. These species are produced in different amounts in the three reaction mixtures at different temperatures, as reported in Fig. 6, in the spectral range 1250–1000 cm^{-1}, where the v(OC) modes can be observed in more detail. The amount of bridged methoxy species (1048 cm^{-1}) is the same in the three reaction mixtures at room temperature (dotted curves in Fig. 6A–C), while the band at 1128 cm^{-1}, related to on top species has a reduced intensity in presence of water and water and oxygen (dotted curves in Fig. 6B and C, respectively) in comparison with the interaction with pure methanol (see dotted curve in Fig. 6A). These results indicate that there is a competition between methanol and water for on top coordination.

We previously tentatively assigned the shoulder at 1157 cm^{-1} to on top methoxy species "modified" by the presence of a vacancy near the site. In a previous work on methanol adsorption on ceria [8], a band at 1160 cm^{-1} was assigned to the ρ(CH$_3$) rocking mode of undissociated methanol. The authors observed this band, together with the bands related to the v(CH$_3$) and v(OC) modes when a large quantity of methanol was adsorbed. We worked with an excess of methanol in all the reactions, as the presence of the intense peak at 1033 cm^{-1} in all the spectra at room
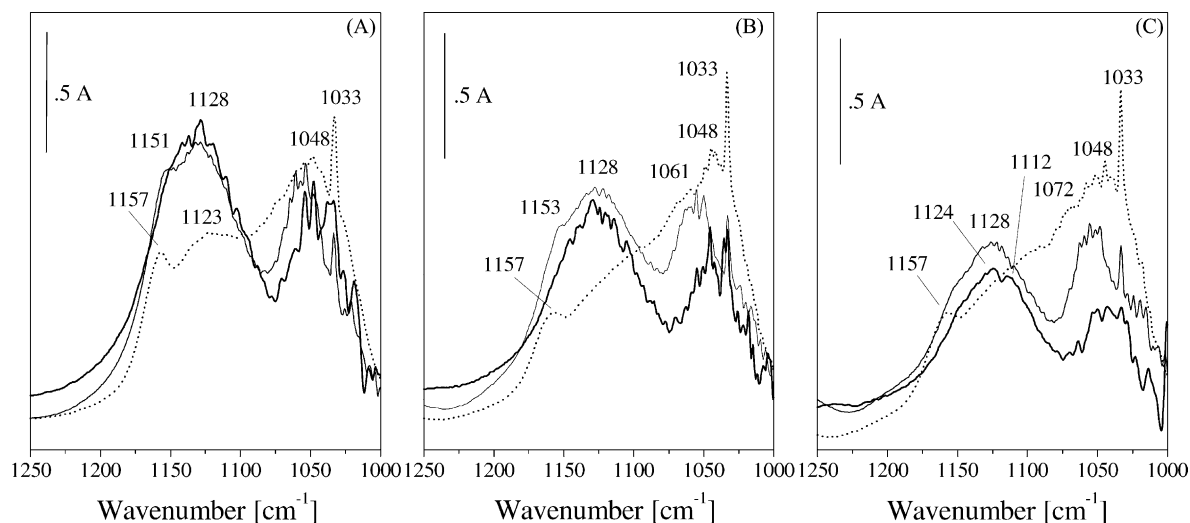
Fig. 6. FTIR absorption spectra obtained by interaction with (A) (m); (B) (mw); and (C) (mwo) on Au/TiO$_2$ at RT (dotted curves), at 403 K (thin curves) and at 473 K (bold curves) in the ν(OC) region.

temperature confirms. This peak always decreases in intensity with the temperature. The band at 1157 cm^{-1} is observed up to 403 K when methanol decomposition and steam reforming are performed (see thin curves in Fig. 6A and B, respectively). This band is detected only at room temperature for the (mwo) mixture, then it is no more detectable (see Fig. 6C). This result can indicate that the methoxy species adsorbed near the vacancies and gold particles react in very mild conditions with oxygen activated on gold near the vacancies, producing formate and formaldehyde on gold sites. The persistence of the 1157 cm^{-1} band even at higher temperatures in the spectra reported in Fig. 6A and B appears as a confirm of the assignment proposed.
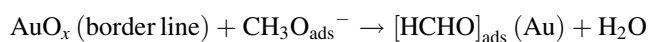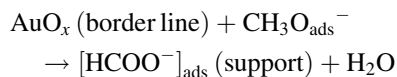
By increasing the temperature up to 403 K (thin curves in the three sections) the bands related to all the on top species have a major intensity, especially for the (m) and (mw) mixtures. Moreover, formate species and formaldehyde adsorbed on gold are produced only when oxygen is present in the reaction mixture (see thin curve in Fig. 2). In this case, both the on top methoxy species are partially oxidized to formate and formaldeyde. It has been already shown previously on other oxides [11] that on top methoxy species were selectively oxidized to formate species. The presence of oxygen in the reaction mixture favors the production of formate species and formaldehyde species already at 403 K. Oxygen stabilizes these species up to 523 K, probably preventing the coke formation.

The bridged methoxy species are stable and slightly decrease only at 473 K in the case of pure methanol decomposition (bold curve in Fig. 6A). These species exhibit a quite similar behavior if we consider the (mw) and (mwo) interactions (bold curves in Fig. 6B and C, respectively) as they decrease with the increase of the temperature. However, water enhances the reactivity of the bridged methoxy species in both cases.

4.2. Mechanisms of the reactions

Similar surface species (mainly methoxy species) in almost the same amounts are detected both in pure methanol and in methanol–water mixtures at 403 K. At this temperature, a reduced amount of methoxy species is detected in presence of oxygen and, at the same time, formate species on the support and formate and formaldehyde on gold are detected. It has been shown previously [12] that active oxygen species are produced by contact with oxygen on Au/TiO$_2$ catalysts. There are some evidences [12] that these species are present in high concentrations at the borderline between the gold particles and the support, where an high concentration of oxygen vacancies on the support is produced during the reduction.

It is well known that on clean UHV conditions methanol is not significantly adsorbed on most copper surfaces, while in presence of oxygen adsorption occurs. One of the principal mechanisms for this activation is a Brönsted base reactivity where highly basic atomic oxygen adsorbed on the metal particles abstracts an acidic hydrogen atom from an adsorbed molecule [13]. These oxygen species can participate to the oxidative dehydrogenation of methanol, producing formate species on the support together with formate and formaldehyde species on the metallic particles, according to the following reactions:

$$AuO_x \, (\text{border line}) + CH_3O_{ads}^{\,-}$$
$$\rightarrow [HCOO^-]_{ads} \, (\text{support}) + H_2O$$

$$AuO_x \, (\text{border line}) + CH_3O_{ads}^{\,-} \rightarrow [HCHO]_{ads} \, (\text{Au}) + H_2O$$

Water allows the oxidation of the methoxy species to formate on the support, starting from 473 K in the (mw) reaction mixture. In fact, by increasing the temperature from 403 up to 473 K, an increase in the amount of this surface intermediate is produced when considering the steam reforming mixture. In autothermal reforming reaction conditions a

decrease of the same species is observed. This opposite behavior is probably related to the endothermic and exothermic character of the two reactions.

In conclusion, in presence of an excess of unreacted methanol in the gas phase, an intensity growth of the formate species and a simultaneous decrease of the methoxy species on the surface have been observed. These data indicates that, in presence of oxygen, there is a direct conversion of methoxy species in formate species adsorbed on gold. The reaction involves methoxy species adsorbed on top on highly uncoordinated titanium sites, adsorbed near oxygen vacancies and near uncoordinated gold sites, where reactive oxygen species can be adsorbed and can participate to the oxidative dehydrogenation reaction to formate species. The formate on gold have a low thermal stability and appears as good intermediates for methanol decomposition at low temperature. The amount of CO could be minimized by lowering the reaction temperature.

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