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Author: Z. Martinez-Ramirez G.A. Flores-Escamilla G.S. Berumen-España S.A. Jimenez-Lam B.E. Handy M.G. Cardenas-Galindo Adan G. Sarmiento-Lopez J.C. Fierro-Gonzalez



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# Methanol Carbonylation Catalyzed by TiO<sub>2</sub>-Supported Gold: An In-Situ Infrared Spectroscopic Investigation

Z. Martinez-Ramirez,<sup>1</sup> G. A. Flores-Escamilla,<sup>1</sup> G. S. Berumen-España,<sup>1</sup> S. A. Jimenez-Lam,<sup>1</sup> B. E. Handy,<sup>2</sup> M. G. Cardenas-Galindo<sup>2</sup>, Adan G. Sarmiento-Lopez<sup>1</sup> and J. C. Fierro-Gonzalez<sup>1\*</sup>

<sup>1</sup>Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Av. Tecnológico y Antonio García Cubas s/n. Celaya, Guanajuato, Mexico 38010.

<sup>2</sup>CIEP, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí. San Luis Potosí, Mexico. 78210.

<sup>\*</sup> Corresponding author. Tel.: +52 4616117575; fax: +52 4616117744. *E-mail address*: jcfierro@iqcelaya.itc.mx (J. C. Fierro-Gonzalez)

#### **Research Highlights**

- TiO<sub>2</sub>-supported gold is active for methanol carbonylation
- Methanol is activated on the support and CO on gold particles
- Methyl iodide promotes the reaction by favoring formation of gold-acetyl intermediate

#### Abstract

TiO<sub>2</sub>-supported gold samples prepared by deposition-precipitation were tested as catalysts for methanol carbonylation to give methyl acetate at atmospheric pressure in the presence of methyl iodide as cocatalyst. Infrared (IR) spectroscopy was used to investigate the reactions of methanol, CO and CH<sub>3</sub>I on the surface of the samples. The results show the formation of methoxy species bonded to Ti<sup>4+</sup> sites upon adsorption of methanol on the supported gold samples. Admission of CO to the flow reactor/IR cell led to the formation of gold carbonyls, which reacted with the surface methoxy species only when CH<sub>3</sub>I was present to give methyl acetate. The data indicate that CH<sub>3</sub>I is necessary to form gold–acetyl species, which are attacked by neighboring methoxy species to give the carbonylation product. Our results show that the methanol carbonylation catalyzed by TiO<sub>2</sub>-supported gold in the presence of CH<sub>3</sub>I occurs by a reaction mechanism that is similar to that occurring on supported Rh catalysts.

Keywords: gold catalysts; methanol carbonylation; infrared spectroscopy.

#### 1. Introduction

Methanol carbonylation is the main route to produce acetic acid and methyl acetate [1]. There are several successful industrial processes for the homogeneous methanol carbonylation using various metals as catalysts, including Rh [1–3], Co [4,5] and Ir [4,5]. In the Monsanto process [2,3] the reaction is catalyzed by a Rh carbonyl complex in solution in the presence of methyl iodide as cocatalyst. There is extensive spectroscopic evidence of reaction intermediates formed during this processs [3,8,9], and the reaction mechanism that has been proposed is widely accepted. However, because the costs associated to the recovery and recycling of the catalyst in solution are relatively high, there is a motivation to prepare solid catalysts that are able to achieve high conversion and selectivity for heterogeneous methanol carbonylation processes.

Supported Rh [10,11], Ni [12,13] and Ir [14,15] catalysts have been used for methanol carbonylation, and it was recently found that supported gold catalysts are also active and selective for the reaction at relatively low temperatures and pressures [16–18]. Goguet et al. [17] investigated the methanol carbonylation catalyzed by carbon-supported gold particles in the presence of methyl iodide as cocatalyst to give methyl acetate. They characterized the samples by X-ray absorption spectroscopy under reaction conditions and found that the presence of methyl iodide promoted the dispersion of gold particles on the support to give  $(Au_2I)^{\delta+}$  or  $(Au_3I_2)^{\delta+}$  surface species, which were proposed to be the active sites for the reaction. Others [19,20] have also reported that methyl iodide favors the dispersion of metal oxide supported gold particles. However, physical evidence of methanol- and CO-derived surface species during methanol carbonylation catalyzed by supported gold has not been reported.

Infrared (IR) spectroscopy has been a valuable tool to investigate the mechanism of methanol carbonylation catalyzed by supported Rh and Ir complexes [11,14]. For example, Haynes et al. [14] measured IR spectra of polymer-supported Rh and Ir carbonyls under reaction conditions and found evidence of surface species that are analogous to those observed during the homogeneous Monsanto process.

To identify possible reaction intermediates during methanol carbonylation we used IR spectroscopy and mass spectrometry to investigate the reactions of methanol, CO and methyl iodide with the surface of TiO<sub>2</sub>-supported gold catalysts. Our results indicate that gold carbonyls, formed upon CO adsorption on the catalysts, react with neighboring surface methoxy species bonded to  $Ti^{4+}$  sites of the support only in the presence of methyl iodide to produce methyl acetate via an Au–acetyl intermediate. The presence of methyl iodide is essential for the reaction to take place at the conditions of our experiments. Our data suggest that the methanol carbonylation catalyzed by  $TiO_{2^-}$  supported gold proceeds by a reaction route that is analogous to those occurring on supported Rh catalysts and in the homogeneous Monsanto process. These results indicate that the  $TiO_2$ -supported gold catalysts are bifunctional, with CO being activated on the gold and methanol being activated on sites of the  $TiO_2$  support. The bifunctional carbonylation [11,14], thus suggesting that it is possible to establish analogies between the way in which supported gold and other supported metals catalyze specific reactions.

#### 2. Experimental

#### 2.1. Synthesis of TiO<sub>2</sub>-supported gold samples

Samples of TiO<sub>2</sub>-supported gold were prepared by deposition-precipitation [21]. TiO<sub>2</sub> powder (Evonik P25) was dried over night at 110 °C prior to the samples syntheses. A solution of HAuCl<sub>4</sub> (Sigma Aldrich) was neutralized with NaOH 1M during stirring and mixed with dry TiO<sub>2</sub> until a pH value of 6 was reached at 60 °C. The resulting mixture was maintained at a pH of 6 and the solid was suction filtered and washed with approximately 1 L of deionized water at 60 °C to give approximately 3 g of TiO<sub>2</sub>-supported gold samples. Finally, the powder was dried at 110 °C for 24 h. The concentration of the HAuCl<sub>4</sub> solution was calculated to give a gold loading of 5.0 wt %.

#### 2.2. Transmission Electron Microscopy

Samples were characterized by high resolution scanning transmission electron microscopy (STEM) on a Phillips TECNAI-F30 HRTEM operated at 300 kV and on a JEOL JEM-2100F instrument operated at 200 kV. Fine sample powder was prepared for analysis by ultrasonic dispersion in ethanol, depositing several drops of the suspension onto copper grids coated with lacey carbon film (Ted Pella). Images were obtained principally in high angle annular dark field (HAADF) mode, and EDX elemental analysis was performed in several areas to confirm the presence of Au particles and estimate the real content of gold on the surface of the samples.

#### 2.3. Temperature-Programmed Reduction

Temperature-programmed reduction (TPR) experiments were performed with a ChemBET instrument (QuantaChrome) that was equipped with a thermal conductivity detector (TCD). Typically, 0.3 g of the TiO<sub>2</sub>-supported gold samples were weighted, loaded into a quartz tube, sealed, and transferred to the characterization system. Prior to each experiment, the samples were pretreated at 110 °C in flowing He [50 mL (NTP) min<sup>-1</sup>] for 20 min to remove adsorbed water. The samples were then treated by heating from 25 to 600 °C at a rate of 10 K min<sup>-1</sup> in a flow of 5 vol % H<sub>2</sub> in Ar. The total gas flow rate was 10 mL (NTP) min<sup>-1</sup>. The experimental parameters were chosen so that the "K number" (defined as the ratio of reducible substance (mol) divided by the H<sub>2</sub> flow rate (mol s<sup>-1</sup>)) had a value in the range between 55 and 140 s. The TCD signal was calibrated to determine H<sub>2</sub> consumptions by using the complete reduction of CuO powder as a standard (Aldrich, 99.995%) and by measuring the area under the TCD signal for known H<sub>2</sub> concentration. The H<sub>2</sub> uptakes were determined with an accuracy of approximately 10%.

#### 2.4. *Methanol carbonylation catalyzed by TiO*<sub>2</sub>-supported gold

Methanol carbonylation catalysis experiments were carried out at atmospheric pressure in a standard once-through nearly isothermal tubular packed-bed flow reactor. Samples of the bare support and of supported gold (25 mg in each case) were loaded into the reactor and treated in a flowing mixture of methanol ( $P_{MeOH} = 109$  Torr), CO ( $P_{CO} = 52$  Torr), methyl iodide ( $P_{CH3I} = 109$  Torr) and He (total flow rate 50 ml (NTP) min<sup>-1</sup> at 760 Torr) at room temperature for 30 min [22]. The temperature of the flow reactor was

increased linearly from room temperature to 400 °C in the presence of the reactive mixture. In other experiments, the TiO<sub>2</sub>-supported gold samples were tested as catalysts for the reaction at constant temperature (200 °C) in the presence of the same reactive mixture. Mass spectra of the effluent gases from the reactor were measured with an online Balzers OmniStar<sup>TM</sup> mass spectrometer running in multi-ion monitoring mode. The changes in the signal intensities of the main fragments of methanol (m/e = 31), methyl acetate (m/e = 43, 74), acetic acid (m/e = 60, 43, 45), dimethyl ether (m/e = 45, 46), CO<sub>2</sub> (m/e = 16, 28, 30, 44) and water (m/e = 18) were recorded [23]. All signals are reported relative to that of the He carrier gas at m/e = 4 to remove any effects of pressure fluctuations. Quantitative analyses of the effluent gases were carried out by using the method reported by Friend et al., [16] which consists of determining the molar fraction of the various compounds as a function of the ion current recorded by the mass spectrometer.

## 2.5. IR spectroscopic characterization of TiO<sub>2</sub>-supported gold samples during methanol adsorption and carbonylation

The TiO<sub>2</sub>-supported gold sample was loaded into a diffuse reflectance Fourier transform (DRIFT) IR cell that was closed and isolated with two standard three-way vacuum valves. IR spectra were recorded with a resolution of 4 cm<sup>-1</sup> with a Nicolet FTIR 6700 spectrometer equipped with a SpectraTech Collector<sup>™</sup> DRIFT attachment fitted with a high-temperature environmental chamber. Each spectrum corresponds to the co-addition of 128 scans. KBr powder was normally used as a reference material. IR spectra were recorded as the sample was exposed to a sequence of treatments in various atmospheres, as follows. First, the sample was treated in a flowing mixture of methanol

 $(P_{MeOH} = 109 \text{ Torr})$  and He (total flow rate 50 ml (NTP) min<sup>-1</sup> at 760 Torr) for 5 min at room temperature. Then, spectra were recorded as flowing CO ( $P_{CO}=$  76 Torr), was admitted to the reactor mixture for 30 min, and finally as a mixture of CO, methanol and CH<sub>3</sub>I was allowed to flow through the sample for 60 min at room temperature. Difference IR spectra of the adsorbed species were obtained by absorption subtraction of the cell and catalyst background spectra using the installed software.

#### 3. Results and Discussion

#### 3.1. Methanol carbonylation catalyzed by TiO<sub>2</sub>-supported gold samples

Mass spectra of the effluent gases from the flow reactor recorded as a sample of TiO<sub>2</sub>-supported gold was treated in the flowing mixture of methanol, CO and methyl iodide at room temperature indicate the formation of methyl acetate, as evidenced by the slight increase in the intensity of the mass fragment at m/e = 74 (Figure 1). The formation of methyl acetate remained nearly constant during approximately 30 min time on stream (TOS). Acetic acid was also formed during the first 5 min TOS, but its mass spectral signal (m/e = 60) then decreased in intensity rapidly and after that time (Figure 1). Acetic acid is also a methanol carbonylation product, and a possible explanation for the decrease of its production is that the partial pressure of methanol was higher than that of the initially adsorbed water on the catalyst. These results indicate that methanol was carbonylated to give methyl acetate and acetic acid even at room temperature in the presence of our gold catalyst. As the temperature of the sample increased, the production of methyl acetate and acetic acid also increased. The intensity of the mass spectral signal of acetic acid reached a maximum value at approximately 120 °C (Figure 1). Then, it

decreased and no acetic acid was detected at temperatures higher than 200 °C. On the other hand, the signal of methyl acetate reached a maximum value at approximately 200 <sup>o</sup>C (Figure 1). At higher temperatures the production of methyl acetate decreased and dimethyl ether was formed, as evidenced by the increase in the intensity of the mass fragment at m/e = 46 (Figure 1). The formation of dimethyl ether increased with increasing temperature until the temperature reached 370 °C, approximately. Above that temperature, the intensity of the mass fragment of dimethyl ether decreased, together with the slight increase in the intensity of the mass fragment of CO<sub>2</sub> at m/e = 44 (Figure 1). Dimethyl ether and CO<sub>2</sub> were probably formed by methanol dehydration [24] and oxidation, respectively. An alternative explanation for the formation of  $CO_2$  is that adsorbed water (or water formed during methanol dehydration) might have reacted with CO via the water-gas shift reaction. Indeed, others [25] have reported that TiO<sub>2</sub>supported gold catalysts are active for the water-gas shift reaction at temperatures that are comparable to those at which CO<sub>2</sub> formation was observed. When the same experiment was performed in the presence of the bare TiO<sub>2</sub> support, no formation of methyl acetate nor acetic acid were observed and only dimethyl ether was produced (Figure 2). Therefore, the results indicate that the presence of gold particles on the TiO<sub>2</sub> favors the methanol carbonylation. The data also show that the formation of dimethyl ether occurred at lower temperature in the presence of the supported gold sample, thus indicating that the gold particles also promote the methanol dehydration. The average diameter of the supported gold particles in the initially prepared sample, as calculated from TEM, was 4.2 nm (Supplementary Data).

To verify that the methanol carbonylation reaction was catalytic, the  $TiO_2$ -supported gold sample was treated in the presence of the reactive mixture at 200 °C for 110 min. Mass spectra of the effluent gases indicate the rapid production of methyl acetate during the first minutes of the treatment, and its signal reached a maximum value after approximately 20 minutes TOS (Figure 3). Then, the production of methyl acetate decreased with increasing TOS until reaching a steady state after approximately 80 min. The calculated rate of production of methyl acetate at steady state was 5.7 mol  $h^{-1} g_{Au}^{-1}$ [26]. This rate was determined by using the real content of gold on the surface of the sample, as determined by EDX (i.e., 3.1 % w/w Au). Under the conditions of our experiments, no acetic acid was detected in the effluent gases from the flow reactor/DRIFT cell. The average diameter of the supported gold particles in a sample after it had been used as catalyst for methanol carbonylation at 200 °C for over 110 min was 6.3 nm (Supplementary Data). These results indicate that the gold particles were aggregated during the catalysis at 200 °C. Furthermore, the particle size distributions of the fresh and used catalysts were significantly different. Thus, it is possible that the decrease in the catalytic activity with increasing TOS (Figure 3) might be associated with the changes in the particle size and distribution of the supported gold particles. Although other variables might also be important, such as build-up of surface iodo species, those species were not detected by EDX characterization of the used catalysts.

#### 3.2. Methanol adsorption on $TiO_2$ and $TiO_2$ -supported gold samples

IR spectra characterizing the bare  $TiO_2$  and  $TiO_2$ -supported gold samples as they were treated in flowing He at room temperature include bands at 3722, 3690, 3665 and

3630 cm<sup>-1</sup> (Figure 4 a and b), assigned to O–H stretching ( $v_{OH}$ ) vibration modes of various types of isolated hydroxyl groups bonded to Ti<sup>4+</sup> sites [27,28]. Spectra also include a broad band centered at approximately 3380 cm<sup>-1</sup> (Figure 4 a and b), assigned to the  $v_{OH}$  vibration mode of hydrogen-bonded hydroxyl groups and/or adsorbed water [27,28]. Admission of methanol to the flow reactor DRIFT cell led to disappearance of the bands at 3690, 3665 and 3630 cm<sup>-1</sup> (Figure 4 c and d), suggesting that the initially present isolated hydroxyl groups participated in the adsorption of methanol [29]. Simultaneously, the broad  $v_{OH}$  band characteristic of hydrogen-bonded hydroxyl groups centered at approximately 3380 cm<sup>-1</sup> became even broader during methanol adsorption (Figure 4 c and d). Thus, it is concluded that methanol was adsorbed molecularly on the sample via hydrogen-bonds with the initially present isolated hydroxyl groups became even broader during methanol adsorption the formation of more hydrogen-bonded hydroxyl groups on the surface of the sample, in agreement with previous reports for the adsorption of methanol and other alcohols on metal oxides [11,31].

Spectra in the C–H stretching ( $v_{CH}$ ) region show bands at 2948 and 2841 cm<sup>-1</sup> (Figure 4 c and d), attributed to the asymmetric and symmetric –CH<sub>3</sub> stretching ( $v_{aCH3}$  and  $v_{sCH3}$ ) modes of molecularly adsorbed methanol [32–35]; and at 2922 and 2818 cm<sup>-1</sup>, assigned to the same vibration modes of methoxy species bonded to TiO<sub>2</sub> [32–35]. In fact, various forms of surface methoxy species bonded to Ti<sup>4+</sup> sites are identified during the experiments, as evidenced by spectra at the region between 1600 and 950 cm<sup>-1</sup> (Figure 5). The bands at 1142 and 1119 cm<sup>-1</sup> (Figure 5) can be assigned to the –CH<sub>3</sub> rocking ( $\rho_{CH3}$ ) and the O–C stretching ( $v_{OC}$ ) vibration modes of linear methoxy species bonded to Ti<sup>4+</sup> sites, respectively [34,35]. The band at 1438 cm<sup>-1</sup> (Figure 5) is assigned to the –CH<sub>3</sub>

bending ( $\delta_{CH3}$ ) mode of methoxy species [34,36] and the band at 1037 cm<sup>-1</sup> can be assigned to the v<sub>CO</sub> vibrations of doubly-bonded methoxy species on Ti<sup>4+</sup> sites [34]. Also, The bands at 1555 and 1357 cm<sup>-1</sup> are assigned to the symmetric and asymmetric COO stretching (v<sub>sCOO</sub> and v<sub>aCOO</sub>) vibration modes of adsorbed formate species, respectively [32,37]. It is possible that formate species were produced by decomposition of some methanol on the surface, as others have reported [38,39]. Finally, the band at 1050 cm<sup>-1</sup> might be assigned to the v<sub>OC</sub> vibration mode of either molecularly adsorbed methanol [34] or surface methoxy species [40].

Therefore, our results indicate that methanol was adsorbed both molecularly and dissociatively on the samples. Because spectra of the TiO<sub>2</sub>-supported gold and those of the bare support include the same bands during methanol adsorption (Figures 4 and 5), it is concluded that methanol-derived surface species were stabilized on sites of the support, and not on the gold particles. This conclusion is consistent with previous reports on the adsorption of various alcohols on supported metal catalysts [11,21,41,42]. A schematic representation of methanol-derived surface species on the TiO<sub>2</sub> and TiO<sub>2</sub>-supported gold samples formed upon methanol adsorption is shown in Figure 6.

## 3.3. Evidence of surface species formed during methanol carbonylation on TiO<sub>2</sub>-supported gold samples at room temperature

With the aim of identifying surface species that were formed during methanol carbonylation, IR spectra were recorded as a  $TiO_2$ -supported gold sample was treated sequentially in various atmospheres as follows: (a) in flowing methanol, (b) in a flowing mixture of methanol and CO and (c) in a flowing mixture of methanol, CO and methyl

iodide at room temperature [43]. The results (Figures 7–9) show that admission of methanol to the flow reactor/DRIFT cell led to the appearance of bands characteristic of methoxy species bonded to  $Ti^{4+}$  sites on the  $TiO_2$ -supported gold samples (i.e., at 2922, 2818,1438, 1142, 1119, and 1037 cm<sup>-1</sup>), as discussed above. When CO was admitted to the cell, the bands assigned to the surface methoxy species did not change (Figures 7 and 8, light gray), thus indicating that the adsorbed alcohol did not react with flowing CO at those conditions. However, a new band appeared at 1260 cm<sup>-1</sup>. The identity of the species responsible for this band is not clear. Toledo-Antonio et al. [44] observed the same band during CO adsorption on  $TiO_2$  nanotubes and assigned to the  $v_{asCOO}$  vibration mode of surface carbonates on metal oxides [45–47]. Those surface species might be formed by the reactive adsorption of CO on the sample.

Simultaneously, spectra at the C–O stretching ( $v_{CO}$ ) region showed the appearance of bands at 2154 and 2105 cm<sup>-1</sup> (Figure 9, light gray) when CO was admitted to the flow reactor/DRIFT cell. The band at 2105 cm<sup>-1</sup> can be attributed to the  $v_{CO}$  vibration mode of CO bonded to zerovalent gold [48–50], and the band at 2154 cm<sup>-1</sup> might be assigned to CO bonded to cationic gold, as others [51–53] have attributed  $v_{CO}$  bands in the range between 2150 and 2200 cm<sup>-1</sup> to those species. It is observed that the intensity of the band characteristic of CO bonded to cationic gold decreased rapidly with increasing TOS, as the intensity of the band assigned to CO bonded to zerovalent gold was reduced to zerovalent gold when CO was present in the feed. Indeed, others have reported that CO is able to reduce supported cationic gold at low temperatures [53,54]. To further investigate the changes

in the oxidation state of supported gold during the various treatments, TPR profiles were measured for the initially prepared sample and for samples that had been exposed to sequential treatments (a) in flowing methanol, (b) in a flowing mixture of methanol and CO and (c) in a flowing mixture of methanol, CO and methyl iodide at room temperature. The results (Figure 10) show the presence of two peaks of H<sub>2</sub> consumption. A low-temperature peak appeared with a maximum at approximately 240 °C for all samples. This peak might be attributed to the reduction of cationic gold present in the samples. Indeed, others [55,56] have observed peaks in the range between 160 and 240 °C in TPR profiles of samples of gold supported on MgO and TiO<sub>2</sub> and have attributed them to the reduction of cationic gold. On the other hand, the high-temperature peak, with maximum value at approximately 430 °C could be attributed to the reduction of surface Ti<sup>4+</sup> atoms to Ti<sup>3+</sup>. Similar peaks have been observed by others [57,58] in TPR profiles of TiO<sub>2</sub>-supported Pt [57] and Au [58] samples. In both cases, it was proposed that Au and Pt particles promote the reduction of surface Ti<sup>4+</sup> sites to Ti<sup>3+</sup>.

Our results indicate that cationic gold was present in the sample ever after it had been exposed to the flow of the various gas mixtures, as the low-temperature peak was always present in the TPR profiles (Figure 10). The area under the low temperature peak in the TPR profile characterizing the sample after it had been treated in methanol (Figure 10b) was essentially the same as that in the TPR profile of the fresh sample (Figure 10a). Thus, it is concluded that methanol did not reduce the supported gold. This observation is consistent with our IR data (Figure 4) showing that methanol was not adsorbed on the gold particles, but on sites on the TiO<sub>2</sub> support. In contrast, the area under the lowtemperature peak decreased significantly for the TPR profile characterizing the sample

that had been treated in the flowing mixture of CO and methanol (Figure 10c). This result is also consistent with our IR data showing that part of the initially present cationic gold was reduced in the presence of flowing CO. Interestingly, the TPR data characterizing the sample after it had been exposed to the flowing mixture of CO, methanol and methyl iodide show that the area under the low-temperature peak increased in intensity (Figure 10d), indicating that the presence of methyl iodide led to the re-oxidation of part of the gold that had been reduced in the presence of flowing CO. Because methyl acetate was formed when methyl iodide was present in the feed, and the TPR results indicate the presence of cationic gold, it could be proposed that cationic gold was be involved in the methanol carbonylation. However, the presence of mixtures of cationic and zerovalent gold sites complicates matters.

IR spectra recorded for the sample in the presence of methyl iodide, CO and methanol indicate various changes (Figures 7–9, dark gray). Bands characteristic of methyl iodide appeared initially at 2978, 2952, 1260 and 1240 cm<sup>-1</sup> (Figures 7 and 8, dark gray). These bands are assigned to the  $v_{aCH3}$ ,  $v_{sCH3}$ ,  $\delta_{aCH3}$  and  $\delta_{sCH3}$  vibration modes, respectively [59,60]. When a TiO<sub>2</sub>-supported gold sample was treated in He saturated with methyl iodide, the same bands appeared (Supplementary Data), thus confirming that they are indeed related to the presence of methyl iodide.

Admission of methyl iodide also caused the rapid disappearance of the  $v_{CO}$  bands characteristic of gold carbonyls, and only the doublet characteristic of gas-phase CO was observed in that region of the spectra (Figure 9, dark gray). This observation indicates the conversion of gold carbonyls in the presence of methyl iodide in the reactive mixture. The consumption of gold carbonyls was simultaneous with the production of methyl

acetate, thus indicating that the gold carbonyls participated in the reaction. Although the bands of both zerovalent and cationic gold carbonyls disappeared when methyl iodide was present in the feed, it is impossible from our data to establish whether only one or both species participated in the catalysis, as the changes in the  $v_{CO}$  region occurred so fast that it only took the time relative to one IR spectrum for those bands to disappear. Our results indicate that the catalyst is bifunctional, with methanol being activated on the TiO<sub>2</sub>, in the form of methoxy species, and CO being activated on the gold. TPR profiles of a sample that had been exposed to a mixture of methanol, CO and methyl iodide at room temperature indicate a higher amount of cationic gold with respect to that observed after the treatment in the flowing mixture of CO and methanol (Figure 10). These results indicate that admission of methyl iodide led to the re-oxidation of part of the supported gold and suggest that cationic gold might be involved in the catalysis.

Concomitant with the disappearance of the  $v_{CO}$  bands, various bands appeared in the spectra in the region between 1600 and 1000 cm<sup>-1</sup> when the sample was treated in the flowing mixture of methanol, CO and methyl iodide (Figure 8, dark gray). The bands at 1465 and 1160 cm<sup>-1</sup> could be assigned to the asymmetric bending and rocking of the OCH<sub>3</sub> group ( $\delta_{aOCH3}$  and  $\rho_{OCH3}$ ) of gas-phase methyl acetate [61–63], respectively. Similarly, the band at 1380 cm<sup>-1</sup> might be assigned to the  $\delta_{sCH3}$  vibration mode of gas-phase methyl acetate [61–63]. Zahidi et al. [60] assigned a band at 1302 cm<sup>-1</sup> to methyl acetate adsorbed on Ni(111). By analogy, we assign the band at 1300 cm<sup>-1</sup> to methyl acetate bonded to the supported gold particles.

These results are consistent with mass spectra of the effluent gases from the flow reactor/DRIFT cell showing the formation of methyl acetate (Figure 1). Our data indicate

that the methanol carbonylation reaction only occurred on the samples when methyl iodide was present in the feed. The need of methyl iodide for the occurrence of methanol carbonylation in the presence of our TiO2-supported gold catalyst suggests that the reaction mechanism might be similar to that occurring in the presence of Rh or Ir catalysts, for which methyl iodide is also used as cocatalyst [3–7]. In those cases, it has been proposed that methyl iodide reacts with the metal to give metal-methyl and metaliodide species [3-7]. Then, CO is inserted into the metal-methyl species to give metalacetyl species. There are reports [64-67] on the formation of surface Pd-acetyl and Ptacetyl complexes from the decomposition of various compounds on Pd(111) and Pt(111), respectively. Those surface complexes are characterized by IR spectra showing  $v_{CO}$ ,  $\delta_{sCH3}$  and  $\rho_{CH3}$  bands in the ranges between 1560–1660, 1318–1355 and 1125–1132 cm<sup>-1</sup>, respectively [64-67]. Our results, showing the appearance of bands at 1580, 1353 and 1130 cm<sup>-1</sup> in the spectra of the supported gold sample as it was treated in the presence of the reactive mixture of methanol, CO and CH<sub>3</sub>I (Figure 8, dark gray), are consistent with the aforementioned examples. Thus, we assign the bands at 1580, 1353 and 1130  $\text{cm}^{-1}$  to the  $v_{CO}$ ,  $\delta_{sCH3}$  and  $\rho_{CH3}$  vibration modes of Au–acetyl complexes formed during catalysis [68]. The presence of these surface species suggests that there might be analogies between methanol carbonylation catalyzed by gold and other metals.

3.4. Role of methyl iodide on the methanol carbonylation catalyzed by supported gold nanoparticles: Analogies between Rh and supported gold catalysts

TEM images characterizing a TiO<sub>2</sub>-supported gold sample after it had been used for methanol carbonylation at room temperature show the presence of gold particles with an average diameter of 3.9 nm (Supplementary Material). This observation indicates that the average size of the gold particles in the sample decreased slightly after it was used as catalyst. Our results are consistent with previous reports showing that metal oxide supported gold particles are re-dispersed when they are exposed to methyl iodide [17-20]. This re-dispersion is thought to occur by the reaction between methyl iodide and surface gold atoms to give segregated gold-iodide species. Chowdhury el al. [70] reported that the reaction between gold films and methyl iodide led to the simultaneous formation of Au–I and Au–CH<sub>3</sub> surface species. Although it is not possible to identify Au-CH<sub>3</sub> surface species from our data, their existence might explain our IR results, as CO bonded to the gold could be inserted rapidly into the gold-methyl bond to give gold-acetyl complexes (as evidenced by the rapid disappearance of the  $v_{CO}$  bands characteristic of gold carbonyls (Figure 9) with the simultaneous appearance of the 1580-, 1353- and 1130-cm<sup>-1</sup> bands (Figure 8) once methyl iodide was admitted to the flow reactor/DRIFT cell). The gold-acetyl species then might undergo a nucleophillic attack by neighboring methoxy species bonded to Ti<sup>4+</sup> sites to give methyl acetate bonded to the gold, which is then desorbed from the sample as the carbonylation product.

The Rh-catalyzed methanol carbonylation is thought to occur by an analogous mechanism, in which Rh<sup>I</sup> complexes undergo the oxidative addition of methyl iodide to give Rh<sup>III</sup> complexes, which then undergo CO insertion to give Rh-acetyl complexes [1,3,7,9]. The mechanism requires the presence of cycles between Rh<sup>I</sup> and Rh<sup>III</sup> complexes. In our case, TPR results show the presence of cationic gold in all samples,

before and after being used as catalysts for methanol carbonylation at room temperature. One could speculate that the apparent analogies between our catalysts and the Rh catalyst might be extended to propose that Au<sup>I</sup> and Au<sup>III</sup> species participate in the methanol carbonylation. Nevertheless, our samples are structurally complex, containing mixtures of zerovalent and cationic gold.

#### 4. Conclusions

In summary, we show that TiO<sub>2</sub>-supported gold catalysts are active for methanol carbonylation to give methyl acetate in the presence of methyl iodide as cocatalyst. Our IR results indicate that methanol is activated on the support (in the form of methoxy species bonded to  $Ti^{4+}$  sites) and CO is activated on the gold particles. The presence of methyl iodide is crucial to allow the formation of gold–acetyl species, which might be attacked by neighbouring surface methoxy species to give methyl acetate. These results suggest that the methanol carbonylation on  $TiO_2$ -supported gold occurs by a route that is analogous to those occurring on other supported metal catalysts. Analogies between the chemistry of gold catalysts and other metals have been proposed for other reactions [71,72]. For example, the group of Corma [71] reported that CeO<sub>2</sub>-supported gold catalysts function similarly to palladium catalysts for the Sonogashira cross-coupling reactions. In that case, the origin of the similarities rested on the fact that Au<sup>1</sup> and Pd<sup>0</sup> have both a  $d^{10}$  electronic configuration. In our case, the analogy between our catalysts and Rh, Ir and Co catalysts for the methanol carbonylation rests on the ability of

supported gold to form carbonyls that react in the presence of methyl iodide to give metal-acetyl species.

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#### Appendix A. Supplementary Data.

Supplementary Data associated with this article can be found in the online version.

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#### **Figure Captions.**

Figure 1. Changes in the intensities of the mass spectral signals of the effluent gases from a flow reactor when the TiO<sub>2</sub>-supported gold sample was treated in (left) flowing He at room temperature, (middle) the flowing reactive mixture of methanol, CO, CH<sub>3</sub>I and He at room temperature and (right) the flowing reactive mixture at increasing temperature. (•) methyl acetate (m/e = 74), (•) acetic acid (m/e = 60), ( $\Delta$ ) dimethyl ether (m/e = 46), and ( $\Box$ ) carbon dioxide (m/e = 44).

Figure 2. Changes in the intensities of the mass spectral signals of the effluent gases from a flow reactor when the bare TiO<sub>2</sub> support was treated in (left) flowing He at room temperature, (middle) the flowing reactive mixture of methanol, CO, CH<sub>3</sub>I and He at room temperature and (right) the flowing reactive mixture at increasing temperature. (•) methyl acetate (m/e = 74), (•) acetic acid (m/e = 60), ( $\Delta$ ) dimethyl ether (m/e = 46), and ( $\Box$ ) carbon dioxide (m/e = 44).

Figure 3. Changes in the intensities of the mass spectral signals of the effluent gases from a flow reactor when the TiO<sub>2</sub>-supported gold sample was treated in the flowing reactive mixture of methanol, CO, CH<sub>3</sub>I and He at 200 °C. (•) methyl acetate (m/e = 74), ( $\Delta$ ) methanol (m/e = 31) and ( $\Box$ ) CO (m/e = 28).

Figure 4. IR spectra characterizing (a) the sample of  $TiO_2$  and (b) the sample of  $TiO_2$ supported gold as they were treated in flowing He; (c) the sample of  $TiO_2$  and (d) the sample of  $TiO_2$ -supported gold as they were treated in methanol and He at room temperature.

Figure 5. Subtraction IR spectra in the region between 1600 and 950 cm<sup>-1</sup> characterizing (a) the bare  $TiO_2$  support and (b) the  $TiO_2$ -supported gold as they were treated in flowing methanol and He at room temperature.

Figure 6. Schematic representation of (a) molecularly adsorbed methanol, (b) linear and (c) doubly-brigded methoxy species bonded to Ti<sup>4+</sup> sites.

Figure 7. IR spectra in the  $v_{CH}$  region recorded as a TiO<sub>2</sub>-supported gold sample was sequentially treated in flowing mixtures of methanol and He (white); methanol, CO and He (light gray); and methanol, CO, CH<sub>3</sub>I and He (dark gray) at room temperature.

Figure 8. Subtraction IR spectra in the region between 1600 and 1000 cm<sup>-1</sup> recorded as a TiO<sub>2</sub>-supported gold sample was sequentially treated in flowing mixtures of methanol and He (white); methanol, CO and He (light gray); and methanol, CO, CH<sub>3</sub>I and He (dark gray) at room temperature.

Figure 9. IR spectra in the  $v_{CO}$  region recorded as a TiO<sub>2</sub>-supported gold sample was sequentially treated in flowing mixtures of methanol and He (white); methanol, CO and He (light gray); and methanol, CO, CH<sub>3</sub>I and He (dark gray) at room temperature.

Figure 10. TPR profiles characterizing the  $TiO_2$ -supported gold sample after it was treated sequentially at room temperature in (a) flowing He for 5 min, (b) a flowing mixture of methanol and He for 30 min, (c) a flowing mixture of methanol, CO and He for 30 min, and (d) a flowing mixture of methanol, CO, methyl iodide and He for 60 min.



Martinez-Ramirez et al. Figure 1



Temperature / °C

Martinez-Ramirez et al. Figure 2



Martinez-Ramirez et al. Figure 3



Martinez-Ramirez et al. Figure 4



Martinez-Ramirez et al. Figure 5



Martinez-Ramirez et al. Figure 6



Martinez-Ramirez et al. Figure 7



Martinez-Ramirez et al. Figure 8



Martinez-Ramirez et al. Figure 9



Martinez-Ramirez et al. Figure 10

#### **Graphical Abstract**

