



# Infrared spectroscopic evidence of adsorbed species during the oxidation of 2-propanol catalyzed by $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported gold: Role of gold as a hydrogen-subtractor

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## ABSTRACT

Samples of gold supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared by deposition–precipitation and tested as catalysts for the aerobic oxidation of 2-propanol to give acetone. IR spectra recorded during catalysis show that the alcohol is first dissociatively adsorbed on the catalysts to form predominantly 2-propoxide species bonded to coordinatively unsaturated Al<sup>3+</sup> sites. It is proposed that gold particles in the proximity of the 2-propoxide species are capable of subtracting hydrogen from the  $\beta$ -C–H bond to give acetone bonded to Al<sup>3+</sup> sites, as evidenced by the appearance of a band at 1704 cm<sup>-1</sup> at a similar temperature as that at which the onset of formation of acetone occurred. Other possible surface reaction pathways are suggested, indicating the interactions of the alcohol with support and metal sites. These results (with a model reaction) might be general and explain the activity of supported gold for the oxidation of other alcohols.

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## 1. Introduction

The selective oxidation of alcohols to aldehydes and ketones is one of the most important reactions in organic chemistry and the search for cost-effective and environmentally benign processes that avoid the use of stoichiometric oxidants, such as permanganate and dichromate has gained great attention [1–3]. An attractive alternative is the use of solid catalysts that are able to perform this reaction in the presence of oxygen at low temperatures and atmospheric pressure.

The discovery by the group of Haruta et al. [4] in the 1980s that gold finely dispersed on metal oxides is highly active for CO oxidation at low temperatures led to a drastic increase in the research of the origin of the activity of a metal that was widely regarded as essentially catalytically inactive. Since then, it has been reported that supported gold catalysts are active for many reactions [5–7], including the selective oxidation of alcohols to ketones and aldehydes [8–11]. Rossi, Prati and coworkers [8,9] were the first to show that supported gold was active for the oxidation of alcohols. They reported that carbon-, Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub>-supported gold samples were excellent catalysts for the oxidation of various diols and carbohydrates [8,9,12]. Since then, it has been reported that supported gold is catalytically active for the selective oxidation of a variety of alcohols, including the oxidation of benzyl alcohol to give ben-

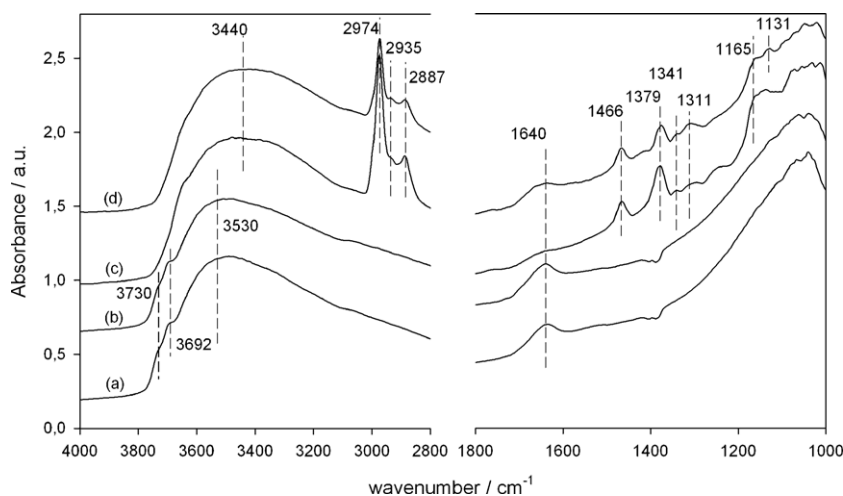
zaldehyde [13], and the oxidation of glucose to give gluconate [14], among other reactions [15].

Although there are numerous reports [5–7] attempting to explain the origin of the catalytic activity of supported gold for CO oxidation, the investigation of reaction mechanisms for the oxidation of alcohols catalyzed by supported gold has only recently received attention. Some authors [16] have suggested that the rate-determining step in the oxidation of alcohols catalyzed by supported gold is the subtraction of hydrogen from the  $\beta$ -C–H bond ( $\alpha$  to the O atom) of the alcohol.

Because some authors have reported that even unsupported gold films and single crystals are active for the oxidation of alcohols [17–19], and because it has been observed that the presence of gold nanoparticles on supports is necessary for the catalysts to be active, it has been assumed that reaction intermediates derived from the alcohol must be bonded to surface gold atoms in supported gold catalysts. Various authors have proposed that during catalysis the alcohol is first dissociated on gold particles to form a surface gold alkoxide, which then reacts to give the oxidation product [1,14,20]. Nevertheless, there is no direct physical evidence of such surface species in typical supported gold catalysts and there is no discussion in the literature regarding the need of their presence for the catalysts to be active.

In the absence of evidence of alcohol-derived species bonded to the supported metal, the debate about the origin of the catalytic activity of supported gold for the oxidation of alcohols has focused on the investigation of the influence of structural variables, including the electronic state of the gold [21], the size of the supported

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**Fig. 1.** IR spectra characterizing (a) the sample of  $\gamma$ - $\text{Al}_2\text{O}_3$  and (b) the sample of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold as they were treated in flowing He; (c) the sample of  $\gamma$ - $\text{Al}_2\text{O}_3$  and (d) the sample of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold as they were treated in flowing 2-propanol,  $\text{O}_2$  and He at room temperature.

particles [22,23] and the nature of the support [24]. However, even investigations that analyze the influence of a single variable provide apparently contradictory results. For example, whereas some authors have suggested that the presence of small gold particles is crucial for the catalysts to be active [22,23], others have found that samples containing relatively large gold particles (i.e., average diameter > 15 nm) are also active [25].

In this work, we report the selective aerobic oxidation of 2-propanol to produce acetone catalyzed by  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold. We focused on the characterization of adsorbed species on the functioning catalysts by means of infrared (IR) spectroscopy. Our results show that 2-propanol is dissociatively adsorbed in the form of 2-propoxide species that are predominantly bonded to Al sites on the surface of  $\gamma$ - $\text{Al}_2\text{O}_3$ . Those species can be oxidized to produce acetone when gold is present on the  $\gamma$ - $\text{Al}_2\text{O}_3$  surface. Our data suggest that the 2-propoxide species can be oxidized in the proximity of gold particles, which provide sites for hydrogen subtraction from the 2-propoxide species. Other possible reaction pathways on the surface of the catalysts are discussed.

## 2. Experimental

### 2.1. Synthesis of $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold samples

Samples of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold were prepared by deposition–precipitation. A solution of  $\text{HAuCl}_4$  (Sigma–Aldrich) was neutralized slowly with vigorous stirring to pH 7 at 60 °C with NaOH 1 M and mixed with  $\gamma$ - $\text{Al}_2\text{O}_3$  (Degussa), which had been dried over night at 120 °C. The resulting mixture was maintained at a pH of 8.0. The mixture was filtered and the solid was washed with deionized water at 60 °C. The solid was suction filtered and then it was dried at 110 °C for 24 h. The concentration of the  $\text{HAuCl}_4$  solution was calculated to give a gold loading of 5.0 wt%.

### 2.2. Infrared spectra characterizing $\gamma$ - $\text{Al}_2\text{O}_3$ and $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold

Samples of the bare support and of supported gold were 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  $\text{cm}^{-1}$  with a Nicolet FTIR 6700 spectrometer equipped with a SpectraTech Collector™ DRIFT attachment fitted with a high-temperature environmental chamber. Spectra were recorded by coadding 128 scans. KBr pow-

der was normally used as a reference material. Difference IR spectra of the adsorbed species were obtained by absorption subtraction of the cell and catalyst background spectra using the installed software.

In the experiments, IR spectra were recorded as each sample (ca. 25 mg) was treated in flowing He (50 ml (NTP)  $\text{min}^{-1}$ ) at atmospheric pressure and room temperature for 30 min. Then, as a flowing mixture of 2-propanol ( $P_{\text{IPrOH}} = 50$  Torr),  $\text{O}_2$  ( $P_{\text{O}_2} = 76$  Torr) and He (total flow rate 50 ml (NTP)  $\text{min}^{-1}$  at 760 Torr) was allowed to enter in contact with the sample at room temperature for 40 min. Finally, the temperature of the cell was increased from room temperature to 300 °C in the presence of the reactive mixture.

### 2.3. Mass spectra characterizing the effluent gases from the flow reactor/DRIFTS cell

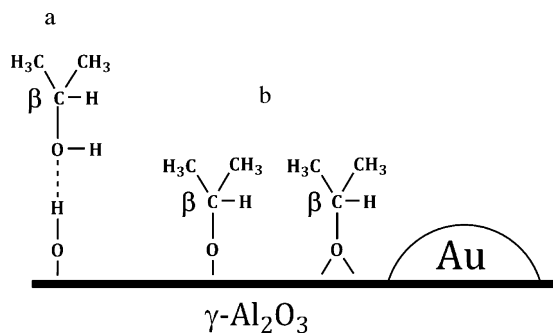
Mass spectra of the effluent gases from the reactor/DRIFTS cell were measured with an on-line Balzers OmniStar™ mass spectrometer running in multi-ion monitoring mode. The changes in the signal intensities of the main fragments of hydrogen ( $m/e = 2$ ),  $\text{H}_2\text{O}$  ( $m/e = 16, 17, 18$ ),  $\text{O}_2$  ( $m/e = 16, 32$ ), 2-propanol ( $m/e = 27, 29, 43, 45$ ), propene ( $m/e = 27, 39, 41, 42, 43$ ), acetone ( $m/e = 15, 27, 43, 58$ ) and  $\text{CO}_2$  ( $m/e = 16, 28, 30, 44$ ) were recorded. All signals are reported relative to that of the He carrier gas at  $m/e = 4$  to remove any effects of pressure fluctuations.

## 3. Results and discussion

### 3.1. Adsorption of 2-propanol on $\gamma$ - $\text{Al}_2\text{O}_3$ and $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold samples at room temperature

IR spectra characterizing the bare  $\gamma$ - $\text{Al}_2\text{O}_3$  and the  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold samples as they were treated in flowing He at room temperature show a shoulder at 3730  $\text{cm}^{-1}$  and a band at 3692  $\text{cm}^{-1}$  assigned to two types of  $(\text{Al})_2\text{OH}$  groups (Fig. 1a and b) [26,27]. Also, the IR spectra of both samples include a broad band centered at approximately 3530  $\text{cm}^{-1}$ , assigned to hydrogen-bonded OH groups [28], and a band at 1640  $\text{cm}^{-1}$ , assigned to adsorbed water.

Exposure of the samples to a flowing mixture of 2-propanol,  $\text{O}_2$  and He at room temperature led to the immediate disappearance of the shoulder at 3730  $\text{cm}^{-1}$  and the band at 3692  $\text{cm}^{-1}$ . This observation is consistent with an interaction of the alcohol with isolated hydroxyl groups of the support. Indeed, the disap-



**Scheme 1.** Schematic representation of (a) 2-propanol molecularly adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (b) 2-propoxide species bonded to cus Al<sup>3+</sup> sites of the support.

pearance of the shoulder at 3730 cm<sup>-1</sup> and the band at 3692 cm<sup>-1</sup> was accompanied by the appearance of a broad band centered at approximately 3440 cm<sup>-1</sup>, which can be attributed to either (a) H-bonded hydroxyl groups on the support [28] formed by interaction of the alcohol with the initially present isolated OH groups and/or (b)  $\nu_{OH}$  vibrations of the adsorbed alcohol (Fig. 1c and d) [26]. Concomitant with these changes,  $\nu_{CH}$  bands at 2974, 2935 and 2887 cm<sup>-1</sup> appeared (Fig. 1c and d). These bands are assigned to  $\nu_{CH_{3as}}$ ,  $2 \times \delta_{CH_{3as}}$  and  $\nu_{CH_3}$  vibrations of the adsorbed alcohol, respectively [26]. These results are consistent with the presence of 2-propanol molecules H-bonded to surface Al–OH groups on both, the bare support and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported gold sample.

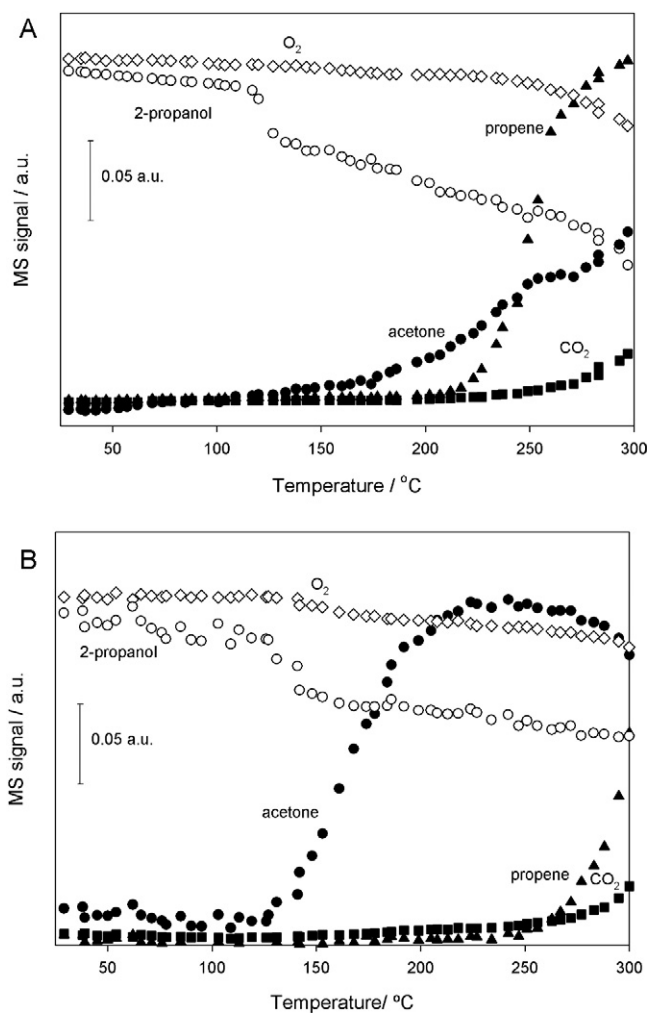
Bands characteristic of 2-propoxide species bonded to coordinatively unsaturated (cus) Al<sup>3+</sup> sites also appeared in the IR spectra of both samples. Frequencies and assignments of these bands are as follows: 1466 cm<sup>-1</sup>,  $\delta_{CH_{3as}}$ ; 1379 cm<sup>-1</sup>,  $\delta_{CH_3}$ ; 1341 cm<sup>-1</sup>,  $\delta_{CH}$ ; and 1165 and 1131 cm<sup>-1</sup>,  $\nu_{CO}/\nu_{CC}$  vibrations (Fig. 1c and d) [26,29]. The appearance of two bands for the  $\nu_{CO}/\nu_{CC}$  vibrations in the IR spectra of the samples is indicative of the presence of linearly- and bridge-bonded 2-propoxide species on cus Al<sup>3+</sup> sites on the surface, as demonstrated by Rossi et al. [30].

These results are in agreement with previous reports [26,29,31] showing the reaction of 2-propanol with surface OH groups on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to produce surface 2-propoxide species at room temperature. Our data are consistent with the presence of two species on the bare support and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported gold sample: (a) 2-propanol molecules H-bonded with OH groups on the support and (b) 2-propoxide species bonded to cus Al<sup>3+</sup> sites (Scheme 1). There are linearly- and bridge-bonded 2-propoxide species on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface.

Because we identify the same IR bands upon adsorption of 2-propanol on the bare support and on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported gold sample, we conclude that the species observed in this work are bonded to Al atoms of the support and not to Au atoms of the supported particles. The lack of evidence of alcohol-derived species bonded to the gold might be explained by (a) their fast reaction to give oxidation or dehydration products, (b) their rapid migration to give surface species bonded to the support or (c) their absence. Because no formation of acetone or propene was observed by mass spectra of the effluent gases from the flow reactor/DRIFTS cell at room temperature, the first possibility is ruled out.

### 3.2. Reactions of 2-propanol and oxygen with the surfaces of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported gold at increasing temperature

Mass spectra characterizing the effluent gases from the reactor/DRIFTS cell that contained a sample of the bare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as it was treated in a flowing mixture of 2-propanol, O<sub>2</sub> and He at increasing temperature show the formation of acetone starting at approxi-



**Fig. 2.** Changes in the intensity of the mass spectral signals of the effluent gases from the flow reactor/DRIFTS cell when (A) the bare support and (B) the sample of Al<sub>2</sub>O<sub>3</sub>-supported gold were treated in a mixture of flowing O<sub>2</sub>, 2-propanol and He at increasing temperatures. (○) 2-Propanol, (◇) oxygen, (●) acetone, (▲) propene and (■) carbon dioxide.

mately 150 °C, as evidenced by a slight increase in the intensity of the signal of the fragment at  $m/e = 43$  (Fig. 2A). The intensity of the signal of acetone increased slowly during the rest of the experiment until the set point (300 °C) was reached. At approximately 220 °C propene started to form, as evidenced by the increase in the intensity of the signal of a fragment at  $m/e = 41$ . The intensity of the signal of propene increased rapidly from that temperature until the set point was reached (Fig. 2A). At approximately 280 °C, formation of CO<sub>2</sub> started, as evidenced by a slight increase in the intensity of the signal at  $m/e = 44$  (Fig. 2A). O<sub>2</sub> and 2-propanol were consumed as the various products formed (Fig. 2A).

These results are in agreement with previous reports showing that 2-propanol can be converted to acetone, propene and CO<sub>2</sub> on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [26,32]. Our data show that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is selective towards the formation of acetone only in the temperature range between 150 and 220 °C under the reaction conditions used in this work. At higher temperatures, 2-propanol reacts to give predominantly the dehydration product (propene) and the total oxidation product (CO<sub>2</sub>). These results are analogous to those of Ermini et al. [32], who observed that 2-propanol decomposed on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to form acetone at approximately 150 °C and propene at approximately 200 °C.

Mass spectra characterizing the effluent gases from the reactor/DRIFTS cell that contained a sample of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold as it was treated in a flowing mixture of 2-propanol,  $\text{O}_2$  and He at increasing temperatures are shown in Fig. 2B. In contrast with the results obtained with the bare support, these data show the formation of acetone starting at approximately  $120^\circ\text{C}$  (Fig. 2B). The formation of acetone increased rapidly with increasing temperature without appreciable formation of propene or  $\text{CO}_2$  (Fig. 2B). At approximately  $250^\circ\text{C}$ , the signal of acetone reached a maximum and it then decreased with increasing temperature until the set point was reached. The decrease of the intensity of the signal of acetone was accompanied by the increase of intensity of the signal of propene (Fig. 2B). At approximately  $280^\circ\text{C}$ ,  $\text{CO}_2$  also started to form (Fig. 2B).

Because acetone formed at lower temperatures when the experiment was done in the presence of the supported gold sample than when it was done in the presence of the bare support, it is concluded that the gold favors the oxidation of 2-propanol to give acetone.

### 3.3. IR spectra characterizing surface species formed during the reactions of 2-propanol and oxygen with the surfaces of $\gamma$ - $\text{Al}_2\text{O}_3$ and $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold at increasing temperature

To investigate the origin of the differences in the catalytic activity of the bare support and the supported gold sample, both samples were characterized by IR spectroscopy during the thermal treatments in the presence of the flowing reactive mixture. The evolution with increasing temperature of IR bands in the spectra recorded as the bare support and the  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold sample were treated in the flowing mixture of 2-propanol,  $\text{O}_2$  and He is shown in Fig. 3. It is observed that bands at  $1735$  and  $1695\text{ cm}^{-1}$  appeared in the IR spectra of the bare  $\gamma$ - $\text{Al}_2\text{O}_3$  at approximately  $150^\circ\text{C}$  (Fig. 3A). Because this temperature is the same as that at which mass spectra of the effluent gases from the reactor/DRIFTS cell indicated the beginning of acetone formation (Fig. 2A), it is expected that they are related to the production of acetone. Indeed, the band at  $1735\text{ cm}^{-1}$  is assigned to the  $\nu_{\text{CO}}$  vibration of gas-phase acetone [26], whereas bands in the range between  $1690$  and  $1702\text{ cm}^{-1}$  have been assigned to the  $\nu_{\text{CO}}$  vibration of acetone molecules bonded to  $\text{cus Al}^{3+}$  sites on aluminum-containing supports [33].

In contrast, when the experiment was done in the presence of the  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold sample, bands attributed to acetone ( $1735$  and  $1704\text{ cm}^{-1}$ ) also appeared in the spectra (Fig. 3B), but at lower temperature (approximately  $125^\circ\text{C}$ ) than when the experiment was done with the bare support. Again, the appearance of these bands occurred at almost the same temperature as that at which formation of acetone was detected by mass spectra of the effluent gases (Fig. 2B). Together with the appearance of the bands at  $1704$  and  $1735\text{ cm}^{-1}$  in the IR spectra of the supported gold sample, sharp bands at  $1570$  and  $1463\text{ cm}^{-1}$ , assigned to surface acetate species appeared (Fig. 3B) [34,35]. A possible pathway for the formation of surface acetates has been proposed to occur through a nucleophilic attack of a surface hydroxyl group on nearby molecules of adsorbed acetone [35].

To test whether the formation of acetone is a true catalytic process, a sample of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold was treated in the flowing mixture of 2-propanol,  $\text{O}_2$  and He at  $200^\circ\text{C}$  for 2 h. The results show the almost immediate formation of acetone when the sample was exposed to the reactive mixture, as evidenced by the rapid increase of the mass spectral signal of acetone (Fig. 4). After its initial increase, the intensity of the signal of acetone decreased with increasing time on stream (TOS) and then it stabilized at a nonzero value after approximately 80 min.

Although it is clear that the presence of gold favors the catalytic formation of acetone, our data do not provide any evidence of sur-

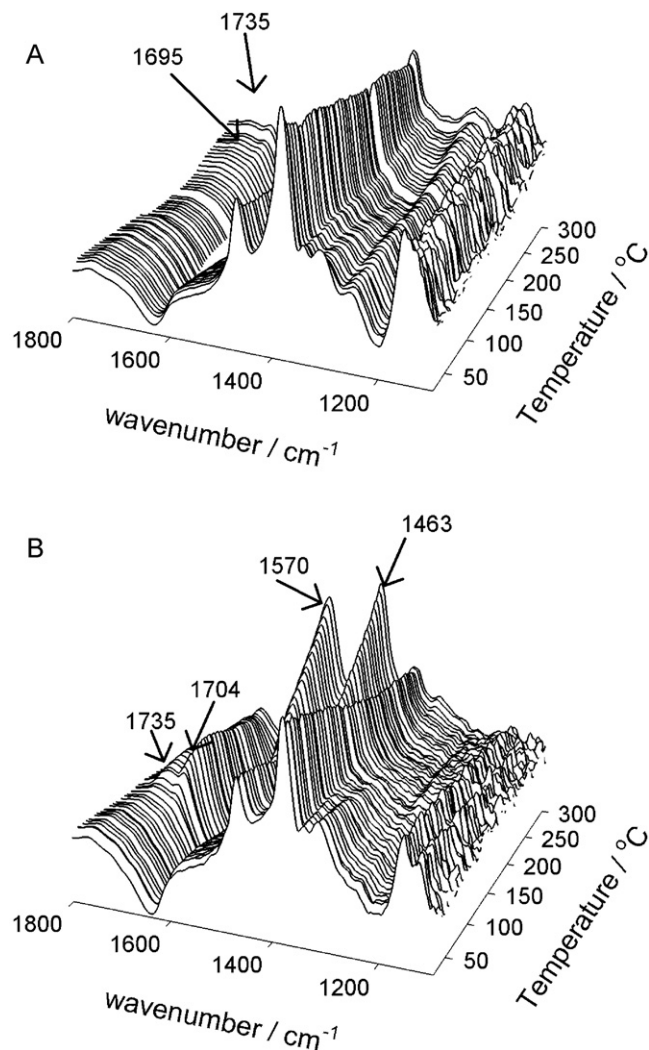


Fig. 3. IR subtraction spectra in the  $1800$ – $1100\text{ cm}^{-1}$  region characterizing (A) the  $\gamma$ - $\text{Al}_2\text{O}_3$  and (B) the  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold sample as they were treated in flowing 2-propanol,  $\text{O}_2$  and He at increasing temperature.

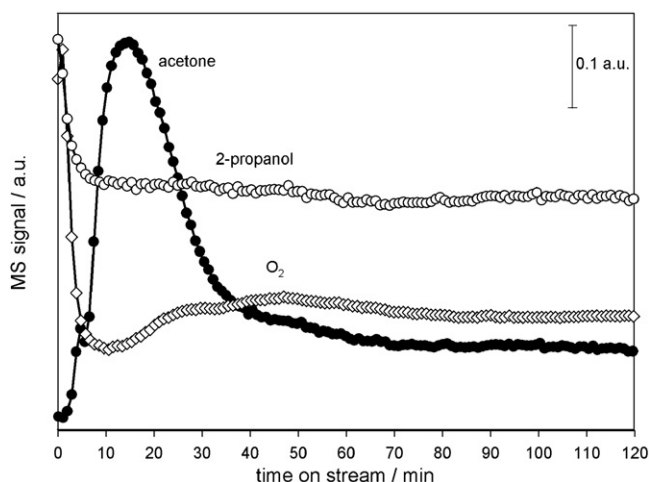
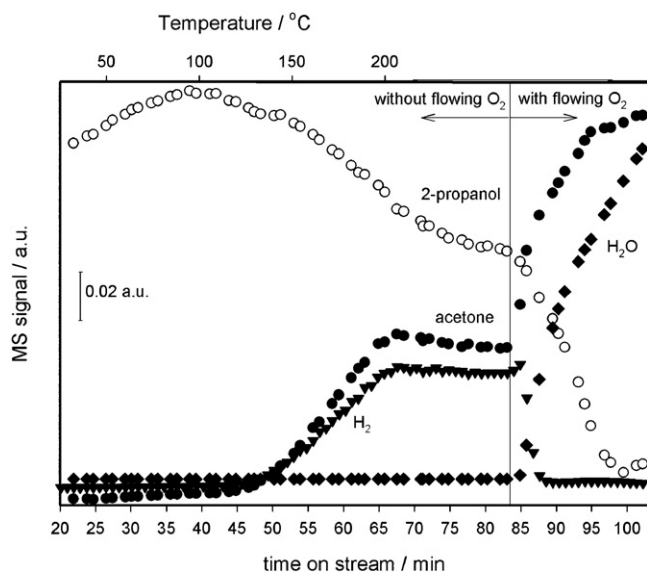


Fig. 4. Changes in the intensity of the mass spectral signals of the effluent gases from the flow reactor/DRIFTS cell when a sample of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold was treated in flowing 2-propanol,  $\text{O}_2$  and He at  $200^\circ\text{C}$ . (○) 2-Propanol, (◇) oxygen, and (●) acetone.





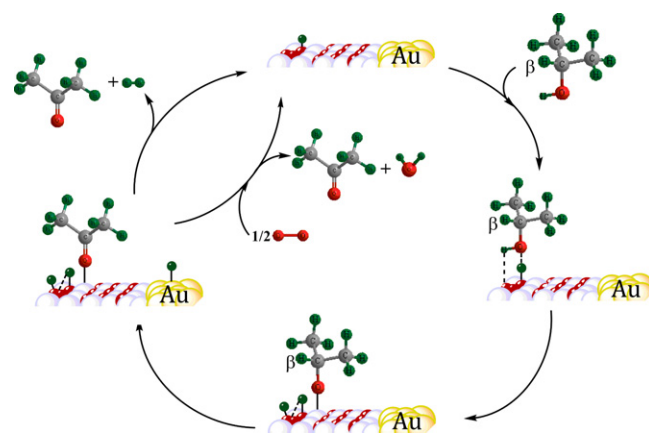
**Fig. 5.** Changes in the intensity of the mass spectral signals of the effluent gases from the flow reactor/DRIFTS cell when a sample of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold was treated in flowing 2-propanol and He as the temperature increased from room temperature to 200 °C, and in the presence of 2-propanol,  $\text{O}_2$  and He at 200 °C. (○) 2-Propanol, (●) acetone, (▼) hydrogen and (◆) water.

face species derived from the alcohol or the acetone directly bonded to the gold. Instead, the IR results show that the alcohol and the acetone are adsorbed on *cus*  $\text{Al}^{3+}$  sites (Fig. 3B). The lack of evidence of alcohol- and acetone-derived species bonded to the gold during catalysis might be explained by (a) the fast reaction of alcohol-derived species bonded to gold to give acetone molecules, which then migrate from gold sites to the support, or (b) the absence of such species. Thus, a question arises for the role of gold in the formation of acetone.

### 3.4. Role of gold as hydrogen-subtractor

Various authors have proposed that metals serve as sites for H-subtraction from C–H bonds of adsorbed molecules [36–38], as well as for the recombinatory desorption of  $\text{H}_2$  [36]. There are many examples showing that metals are capable of subtracting hydrogen from organic species that are bonded to neighboring sites on supports. Some examples include the conversion of cyclohexane to benzene catalyzed by  $\text{Al}_2\text{O}_3$ -supported  $\text{MoO}_x$  [39], aldol condensation reactions of ethanol catalyzed by NiO- and MgO-supported Cu [40,41], and the dehydrogenation of *n*-alkanes catalyzed by carbon-supported Pt [42]. In all cases, it was shown that C–H activation occurs on the support, whereas H-adatoms are removed by neighboring metal sites that catalyze their recombinative desorption to form  $\text{H}_2$  molecules. Thus, one can hypothesize that a similar reaction pathway might occur during the oxidation of 2-propanol catalyzed by  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold. Such a pathway might explain the absence of alcohol- and acetone-derived species bonded to gold during catalysis.

To test whether the gold facilitates hydrogen subtraction by cleavage of the  $\beta$ -C–H bond of the surface 2-propoxide species (Scheme 1), a sample of  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold was treated (in the absence of  $\text{O}_2$ ) with a flowing mixture of He and 2-propanol as the temperature increased linearly from room temperature to 200 °C. Mass spectra characterizing the effluent gases from the flow reactor/DRIFTS cell show that acetone started to form during the thermal treatment at approximately 135 °C, with the concomitant formation of  $\text{H}_2$  (Fig. 5). The intensities of the signals of acetone and  $\text{H}_2$  increased with increasing temperature until the set point



**Scheme 2.** Schematic representation of the catalytic cycle for the oxidation of 2-propanol over  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold.

(200 °C) was reached. After approximately 20 min TOS at 200 °C in the presence of flowing 2-propanol and He, the signals of acetone and  $\text{H}_2$  remained nearly constant. These results indicate that the gold facilitates the cleavage of the  $\beta$ -C–H bond of the surface 2-propoxide species to form acetone and  $\text{H}_2$  in the absence of  $\text{O}_2$ . When the same experiment was done in the presence of the bare  $\gamma$ - $\text{Al}_2\text{O}_3$ , no formation of acetone or hydrogen were observed (Supplementary Data). Cleavage of the  $\beta$ -C–H bond could lead to the formation of a gold hydride. Although we have no direct evidence of such species, a recent report provides electron paramagnetic resonance (EPR) spectroscopic and spin trapping evidence of gold hydrides during the oxidation of secondary alcohols catalyzed by supported gold [43]. In the absence of  $\text{O}_2$ , hydrogen atoms bonded to gold might recombine to give  $\text{H}_2$ , which explains the detection of  $\text{H}_2$  in mass spectra of the effluent gases from the reactor (Fig. 5).

When flowing  $\text{O}_2$  was admitted to the reactor/DRIFTS cell at 200 °C, the concentration of acetone in the effluent gases increased drastically, and the concentration of  $\text{H}_2$  decreased. Concomitant with these changes, formation of  $\text{H}_2\text{O}$  was observed (Fig. 5). These results suggest that  $\text{O}_2$  reacts with the gold hydrides to give  $\text{H}_2\text{O}$ , leaving surface gold atoms ready to remove more hydrogen atoms from the  $\beta$ -C–H bond of the surface 2-propoxide species. Possible pathways for the formation of acetone from 2-propanol in the absence and in the presence of flowing  $\text{O}_2$  are shown in Scheme 2. It is emphasized that this proposal does not require the alcohol to be bonded to the gold, but to *cus*  $\text{Al}^{3+}$  sites, which are expected to be in the proximity of gold particles. The role of gold is crucial, providing sites for the removal of hydrogen from the  $\beta$ -C–H bond of the surface 2-propoxide species. Communication between the support and the gold sites might be accomplished by surface diffusion of hydrogen atoms [36], as it has been proposed for many examples in which other supported metals subtract hydrogen from C–H bonds [39–42].

### 3.5. Other possible reaction pathways for the oxidation of 2-propanol catalyzed by $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold

Because there are reports [17–19] showing that unsupported gold is active for the oxidation of alcohols, the possibility of the existence of alcohol- and acetone-derived species bonded to the gold in our  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported gold samples during catalysis cannot be completely ruled out. Some experiments done with unsupported gold have shown that the oxidation of alcohols proceeds on gold surfaces when they are precovered with atomic oxygen [17,18]. Although no physical evidence of surface species has been reported, this observation has been explained in terms of the Brønsted-base

character of oxygen adatoms on the group 1B metals, which induces the abstraction of acidic hydrogen from alcohols to give metal alkoxides. The alkoxide species might then be oxidized to produce ketones or aldehydes [19,44]. In principle, this rationale could be extended to explain what might happen on typical supported gold catalysts.

Therefore, in addition to the reaction pathway shown in Scheme 2, oxygen activated on gold atoms at the perimeter of the supported gold particles could oxidize molecularly adsorbed 2-propanol and/or 2-propoxide species bonded to either gold atoms or to the support to give acetone.

### 3.6. Implications for oxidation of other alcohols catalyzed by supported gold

There are many reports of the supported gold-catalyzed oxidation of various alcohols, including benzyl alcohol [1,3,13], and glucose [14,45]. To explain the activity of the catalysts, most authors have assumed that the alcohol is first adsorbed on the gold and it then reacts to give aldehydes, ketones and/or CO<sub>2</sub>. Although the assumption is consistent with the catalytic activity of unsupported gold for the oxidation of alcohols, there is no physical evidence for the direct adsorption of the alcohol on the gold and no discussion about the need for that adsorption to occur for typical supported gold catalysts to be active. The question that arises is whether our results, indicating that the activation of 2-propanol occurs predominantly on sites of the support, can be generalized to explain the oxidation of other alcohols catalyzed by supported gold.

Recently, Rousseau et al. [46] reported the total oxidation of methanol catalyzed by CeO<sub>2</sub>-supported gold to give CO<sub>2</sub>. They proposed that the alcohol was adsorbed on the CeO<sub>2</sub> surface in the form of methoxy species, which were transformed into formates bonded to Ce<sup>3+</sup> sites. The oxidation of the formates to give CO<sub>2</sub> was proposed to be the rate-determining step for the reaction. Our results, showing that 2-propanol is predominantly adsorbed on the support in the form of 2-propoxide species, are in agreement with those of Rousseau et al. [46]. Our data indicate that the gold provides the surface with the necessary hydrogen-abstraction sites, facilitating the cleavage of the β-C–H bond of surface 2-propoxide species to form acetone adsorbed on *cus* Al<sup>3+</sup> sites (Scheme 2). This reaction path is analogous to a previous proposal for the dehydrogenation of 2-propanol catalyzed by Al<sub>2</sub>O<sub>3</sub> modified with Ni, Rh and Pt particles [26], and more generally to proposals invoking the catalytic subtraction of hydrogen from C–H bonds by supported metals in various reactions [39–42].

## 4. Conclusions

We prepared a γ-Al<sub>2</sub>O<sub>3</sub>-supported gold catalyst that is active for the aerobic oxidation of 2-propanol to give acetone. Our IR data, characterizing the catalyst in its functioning state, provide evidence showing that 2-propanol is bonded predominantly to *cus* Al<sup>3+</sup> in the form of surface 2-propoxide species. The role of gold consists of providing the necessary sites for hydrogen subtraction from the β-C–H bond of the surface 2-propoxides to give acetone bonded to *cus* Al<sup>3+</sup> sites, which is then desorbed. Our results, showing that adsorption of the alcohol occurs predominantly on the surface of the support might be generalized to explain the oxidation of other alcohols catalyzed by supported gold. We acknowledge, however, that other pathways involving the presence of alcohol- and acetone-derived species bonded to either the gold or the support and their reactions with activated oxygen are also possible. The issues of oxygen acti-

vation on supported gold catalysts for oxidation reactions still need resolution.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.05.001.

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