

# Promotion by sulfur of gold catalysts for crotyl alcohol formation from crotonaldehyde hydrogenation

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**Thiophene doping of supported gold catalysts increases the rate of formation of the unsaturated alcohol for the hydrogenation of the  $\alpha,\beta$ -unsaturated aldehyde, crotonaldehyde, providing the first example of the promotion of gold by sulfur.**

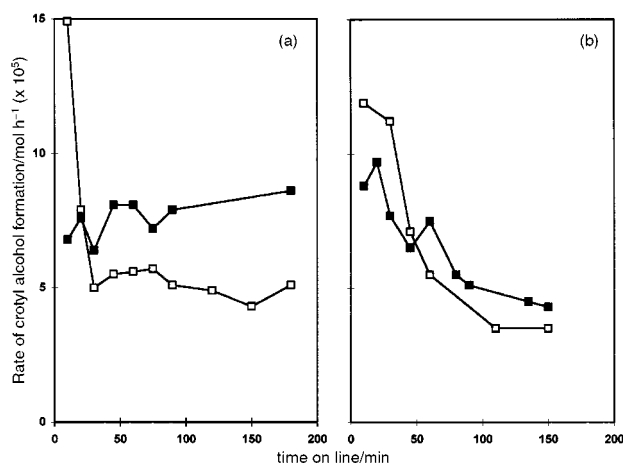
During the last decade the use of gold as a heterogeneous catalyst has been the subject of renewed interest, with most research being directed at oxidation reactions, particularly the room temperature oxidation of carbon monoxide.<sup>1,2</sup> The activity of such catalysts has been associated with the existence of sites at the gold-support interface where an intimate contact between the small hemispherical gold particles (< 6 nm) and the support exists.<sup>1</sup> Relatively little attention has been given to the development of Au-based hydrogenation catalysts and in addition there have been no studies concerning the role of promoters or additives with gold catalysts. Most previous studies of Au as hydrogenation catalysts involve relatively simple molecules such as CO and CO<sub>2</sub><sup>3-5</sup> and alkenes,<sup>6</sup> whereas there are only a very limited number of reports of selective hydrogenation of multifunctional organic molecules.<sup>7,8</sup> Molecules such as  $\alpha,\beta$ -unsaturated aldehydes, ketones and esters are difficult to hydrogenate with high selectivity to the corresponding unsaturated alcohols. However, these reactions are of considerable importance in many areas of the chemical industry, often being employed in the manufacture of fine chemicals, pharmaceuticals and fragrances. For example, crotyl alcohol is currently produced using stoichiometric hydrogen donors and an improved catalytic process would be advantageous. Many studies<sup>9-14</sup> of the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes and ketones have tried to gain fundamental information on selectivity control in these reactions by using different approaches in attempts to design and develop suitable catalysts.

The present work shows that supported Au catalysts, when appropriately prepared, can be highly selective for the formation of unsaturated alcohols, and furthermore, pre-treatment of supported Au catalysts with thiophene can improve the selectivity to crotyl alcohol in the hydrogenation of crotonaldehyde, whilst also maintaining catalytic activity.

ZnO and ZrO<sub>2</sub> supported Au (5 wt% Au<sup>0</sup>) were prepared by a co-precipitation technique and Au/SiO<sub>2</sub> was prepared by impregnation. † Reactions were carried out in a continuous flow, fixed-bed, micro-reactor at atmospheric pressure (weight hourly space velocity = 0.7 h<sup>-1</sup>, H<sub>2</sub> : crotonaldehyde = 14:1) using on-line GC analysis. The catalysts (200 mg) were reduced *in situ* in a flow of hydrogen at 250 °C for 1 h. Crotonaldehyde was fed into the system by means of a calibrated syringe pump into a flow of hydrogen. Modification of the catalyst was achieved *via* direct injection of 0.5  $\mu$ l thiophene into a flow of hydrogen with the catalyst at 250 °C after reduction.

The results obtained for the hydrogenation of crotonaldehyde at 250 °C over unmodified and thiophene-treated samples are given in Table 1. After an initial stabilisation period, both Au/ZnO and Au/ZrO<sub>2</sub> catalysts display similar activities while the Au/ZnO is more selective for C=O bond hydrogenation to give crotyl alcohol. Both Au/ZnO and Au/ZrO<sub>2</sub> when modified by sulfur, after initial stabilisation, give much higher rates of synthesis of crotyl alcohol when compared to the undoped

catalyst (Fig. 1). It is also observed that the rate of butanal formation is maintained when Au/ZnO is modified by sulfur and is slightly decreased for the reaction over sulfur modified Au/ZrO<sub>2</sub>. However, when sulfur modification of silica supported Au is examined, it is observed that sulfur effectively decreases the rate of hydrogenation as would usually be expected. This indicates that the nature of the oxide support is of importance to observe this rate enhancement. It is suggested from these observations that sites present on the surface of ZnO and ZrO<sub>2</sub> supported catalysts are very different in nature to those available at the surface of Au/SiO<sub>2</sub>. Examination of the Au particle size for the catalysts has been carried out using both X-ray line broadening and transmission electron microscopy. For catalysts prepared by co-precipitation, the Au particles are typically 2–4 nm in size. However, the catalysts prepared by impregnation exhibit much larger particle sizes (typically > 150 nm). It is this difference in particle size which we consider to be important and the high catalytic activity and selectivity of Au catalysts is associated with small Au particles.



**Fig. 1** Effect of thiophene addition on the rate of crotyl alcohol formation (mol h<sup>-1</sup> × 10<sup>5</sup>) over (a) Au/ZnO and (b) Au/ZrO<sub>2</sub>: (□) Unmodified, (■) Thiophene treated.

An Au/ZnO catalyst was also prepared by impregnation and subjected to the same reduction and reaction treatments as the Au/ZnO catalysts prepared by co-precipitation. The catalyst prepared by impregnation was found to be inactive in the hydrogenation of crotonaldehyde, emphasising that the method of preparation of Au/ZnO is crucial for this reaction system.

For Au/ZnO it was observed that increasing the temperature of reduction from 250 to 400 °C resulted in a progressive increase in selectivity to crotyl alcohol (reaching a maximum of 82% for Au/ZnO reduced at 400 °C) without major loss of activity. This selectivity is much higher than previous literature data for this reaction.<sup>11-14</sup>

Initial characterisation of these systems by *in situ* FTIR studies of CO adsorption have been performed. ‡ CO adsorption on reduced, unmodified, Au/ZnO prepared by co-precipitation produced a band at 2035 cm<sup>-1</sup> at low CO coverages which shifted to 2045 cm<sup>-1</sup> as the amount of CO adsorbed was increased. This band has been tentatively assigned to CO

**Table 1** Crotonaldehyde hydrogenation at 250 °C over unmodified and thiophene-treated 5 wt% Au catalysts

| Catalyst              | t/min | Conv. (%) | Selectivity (%) <sup>a</sup> |      |      |     |      | Others |
|-----------------------|-------|-----------|------------------------------|------|------|-----|------|--------|
|                       |       |           | B-AL                         | C-OL | B-OL | 2EH | 2E2H |        |
| Au/ZnO                | 10    | 41.4      | 43.8                         | 29.7 | 10.7 | 4.6 | 2.1  | 9.1    |
|                       | 30    | 8.7       | 37.8                         | 47.8 | —    | —   | 0.9  | 13.5   |
|                       | 60    | 8.9       | 35.1                         | 51.7 | —    | —   | —    | 13.2   |
|                       | 180   | 7.8       | 34.1                         | 54.1 | —    | —   | 1.1  | 10.7   |
| S-Au/ZnO              | 10    | 27.9      | 44.5                         | 20.0 | 15.8 | 1.5 | 1.6  | 16.6   |
|                       | 30    | 9.3       | 32.3                         | 56.6 | —    | —   | —    | 11.1   |
|                       | 60    | 11.1      | 29.6                         | 60.6 | —    | —   | —    | 8.8    |
|                       | 180   | 10.9      | 26.8                         | 65.4 | —    | —   | —    | 7.8    |
| Au/ZrO <sub>2</sub>   | 10    | 30.4      | 45.1                         | 32.5 | 13.7 | 2.7 | —    | 5.9    |
|                       | 30    | 18.2      | 38.8                         | 50.9 | 5.1  | —   | —    | 5.2    |
|                       | 60    | 12.0      | 49.1                         | 38.2 | 5.9  | —   | —    | 6.9    |
|                       | 150   | 9.2       | 54.5                         | 32.1 | 7.1  | —   | —    | 6.3    |
| S-Au/ZrO <sub>2</sub> | 10    | 21.3      | 42.3                         | 34.3 | 13.3 | 7.8 | —    | 2.3    |
|                       | 30    | 14.2      | 37.9                         | 44.6 | 7.2  | 8   | —    | 2.3    |
|                       | 60    | 12.2      | 40.8                         | 50.8 | 5.9  | —   | —    | 2.5    |
|                       | 150   | 7.5       | 44.5                         | 47.8 | 4.8  | —   | —    | 2.9    |
| Au/SiO <sub>2</sub>   | 10    | 11.2      | 96.2                         | —    | —    | —   | —    | 3.8    |
|                       | 30    | 23.2      | 97.7                         | —    | —    | —   | —    | 2.3    |
|                       | 60    | 21.9      | 97.9                         | —    | —    | —   | —    | 2.1    |
|                       | 180   | 21.6      | 97.8                         | —    | —    | —   | —    | 2.2    |
| S-Au/SiO <sub>2</sub> | 10    | 8.6       | 98.2                         | —    | —    | —   | —    | 1.8    |
|                       | 40    | 11.9      | 98.6                         | —    | —    | —   | —    | 1.4    |
|                       | 60    | 13.3      | 98.5                         | —    | —    | —   | —    | 1.5    |
|                       | 180   | 14.6      | 98.4                         | —    | —    | —   | —    | 1.6    |

<sup>a</sup> B-AL = butanal, C-OL = crotyl alcohol, B-OL = butan-1-ol, 2EH = 2-ethylhexanal, 2E2H = 2-ethylhex-2-enal, Others = butane and trace C<sub>3</sub> molecules. S-prefix indicates thiophene modified sample.

adsorbed on Au defect sites or isolated Au atoms in the support matrix. Preadsorption of thiophene at 250 °C caused this band to shift to higher wavenumbers by 15 cm<sup>-1</sup> and a shift of similar magnitude to higher wavenumbers was again observed as the CO coverage increased. This shift, which we consider to be electronic in nature, provides evidence for the direct modification of the Au surface by thiophene or products of thiophene adsorption.

One possible explanation of the superior catalytic performance of the Au/ZnO and Au/ZrO<sub>2</sub> catalysts, compared to the Au/SiO<sub>2</sub> system, can be based on the work of Haruta,<sup>1,2</sup> concerning CO oxidation, that when Au catalysts are prepared by co-precipitation the support can provide interfacial sites adjacent to hemispherical Au particles that are involved in the activation of reactants, either alone or in association with nearby Au sites. In this case, the presence of sites at the Au-support interface on Au/ZnO and Au/ZrO<sub>2</sub> surfaces could be responsible for the preferential activation of the carbonyl function to hydrogenation. Obviously, such interfacial sites would not then be present on the Au/SiO<sub>2</sub> since no crotyl alcohol was detected. This could be due to the presence of larger, less strongly bonded particles which are more spherical in shape as is often observed with Au catalysts prepared by impregnation. The effect of thiophene may therefore be to electronically modify these interface sites in such a way as to improve activation of the carbonyl group or alternatively to create new active sites by the modification of non-interfacial sites.

We consider these results are the first observation of a promotional effect of sulfur for a Au catalyst. It is clear that the observed promotion is dependent on the nature of the preparation method and the oxide support. We have made no attempt to optimise the rate enhancement and it can be expected that further improvements can be observed by appropriate modification of the experimental conditions and catalyst design. We thank the EPSRC and Syntex for financial support. We also acknowledge C. H. Rochester, J. A. Anderson and H. A. Abdullah of Dundee University for *in situ* FTIR studies.

## Notes and references

† Au/ZnO and Au/ZrO<sub>2</sub> were prepared by mixing solutions of Zn(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O or Zr(O)(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O with HAuCl<sub>4</sub> solution, which all

contained calculated amounts of Zn, Zr and Au salts required to give a 5 wt% loading of Au<sup>0</sup> on ZnO or ZrO<sub>2</sub>. The mixed solutions were heated to 80 °C and 1 M Na<sub>2</sub>CO<sub>3</sub> solution was added with continual stirring until a pH of ca. 9 was reached. The precipitate was then aged for 20 min prior to vacuum filtration, washing with approximately 1 l of hot deionised H<sub>2</sub>O and drying overnight at 110 °C. The samples were then calcined at 400 °C for 4 h in static air. The Au/SiO<sub>2</sub> catalyst was prepared by adding the required amount of silica (Cab-O-sil M5) to a solution containing a calculated amount of HAuCl<sub>4</sub> to give a 5 wt% loading of Au<sup>0</sup>. The mixture was allowed to evaporate to dryness at 80 °C (approximately 5 hours) with continual stirring after which the residual cake was dried overnight at 110 °C and calcined at 300 °C for 4 h in static air.

‡ A catalyst disc was mounted in a glass IR cell linked to a vacuum line and reduced *in situ* in a flow of hydrogen at 250 °C for 1 h. The sample was then cooled to room temperature and exposed to increasing pressures of CO and FTIR spectra were recorded after each addition of CO. For modified samples, a low level (< 1 mm Hg) of thiophene was admitted to the sample at 250 °C immediately after reduction. The sample was then cooled to room temperature and CO adsorption was performed and monitored by FTIR spectroscopy as before.

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