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Hydrogenation of but-2-enal over supported Au/ZnO catalysts

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The hydrogenation of but-2-enal over supported Au catalysts is discussed, together with a detailed characterisation study using X-ray diffraction, infrared spectroscopy and transmission electron microscopy. Au/ZnO catalysts are found to be selective for the formation of the unsaturated alcohol, but-2-en-1-ol rather than the saturated aldehyde, butanal. In general, the addition of thiophene is found to enhance the yield of the unsaturated alcohol. Detailed transmission electron microscopy and infrared spectroscopy studies show that thiophene modification of Au/ZnO catalysts does not affect the Au-particle size or morphology; rather, thiophene undergoes irreversible dissociative adsorption giving a surface in which the Au sites are electronically promoted by sulfur. It is observed that thiophene modification does not give any marked effect on catalyst performance for the catalysts that contain large Au-particles ($\geqslant 10$ nm) and, hence, it is considered that the sulfur promotion observed is associated with smaller Au nanoparticles. The highest but-2-en-1-ol selectivities ($\sim 80\%$) are observed for 5 wt.% Au/ZnO catalysts reduced at 400 °C prior to reaction. It is proposed that the origin of high selectivity is associated with large Au particles (10–20 nm in diameter) that are present in this catalyst.

Introduction

The use of gold as a heterogeneous catalyst has received significant attention in recent years.[1] For a considerable time, gold had been considered to be a metal of limited application as a catalyst and, indeed, had been used as an inert diluent in some catalytic systems.[2] The renewed interest in gold as a heterogeneous catalyst comes from the observation that gold is a catalyst of choice for two reactions. First, it was initially predicted[3] and subsequently demonstrated[4,5] that gold would be the most active catalyst for the hydrochlorination of ethyne. Subsequently, Haruta and co-workers[6,7] have shown that supported gold catalysts were highly effective for the oxidation of carbon monoxide at ambient conditions and even at temperatures as low as −76 °C. The observation of catalytic activity for oxidation by molecular oxygen at such low temperatures has prompted a massive body of recent research[1] and selective oxidation reactions have also now been reported, *e.g.* Au/TiO_2 for the oxidation of propene to methyl oxirane.[8] In addition, Au/α-Fe_2O_3, is a more active catalyst for the water-gas shift reaction at lower temperature than the CuO/ZnO catalysts that are used commercially.[9]

Although gold is now being extensively investigated for both selective and total oxidation reactions, there has been much less attention given to the activity and selectivity of selected gold catalysts for hydrogenation reactions. Couper and Eley[10,11] demonstrated that gold surfaces could convert *para*-hydrogen to *ortho*-hydrogen. A number of studies also showed that both gold foil[12,13] and supported gold catalysts[14–16] are active for H_2–D_2 exchange reactions at temperatures above 200 °C. These early studies demonstrated clearly that gold surfaces can activate hydrogen. Subsequent studies confirmed that gold can catalyse the hydrogenation of linear alkenes,[15–18] cyclohexene,[19,20] alkynes,[16,21] benzene[22] and also acetone to isopropanol.[23] Sermon *et al.*[16] found that Au/γ-Al_2O_3 catalysts containing less than 5% Au were inactive for the hydrogenation of pent-1-ene, but very different results were obtained using Au/SiO_2 catalysts. When hydrogen was present in massive excess, low concentrations of Au supported on SiO_2 were active for pent-1-ene hydrogenation and the maximum activity was observed at 0.04 wt.% Au. This observation indicates that hydrogenation reactions may be sensitive to both Au particle size and the nature of the support, as has been observed with oxidation reactions.[6,7]

In a prior communication, we have shown[24] that supported catalysts are selective for the hydrogenation of but-2-enal to form the unsaturated alcohol but-2-en-1-ol. Furthermore, we demonstrated that this selectivity could be enhanced by pretreatment of the supported gold catalysts with thiophene. In this paper, we extend these earlier studies and show that the particle size of Au is an important factor in the control of this reaction selectivity. The observation of a promotional effect of low levels of sulfur was based on our earlier studies using Cu/γ-Al_2O_3 catalysts.[25–27]

Experimental

Catalyst preparation

A series of ZnO supported Au catalysts with Au metal loadings of 0.25, 0.5, 1. 2, 5 and 10 wt.%, were prepared by coprecipitation according to the following procedure. A mixed

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solution of $Zn(NO_3)_2 \cdot H_2O$ (Aldrich, 99.999%) and $HAuCl_4 \cdot H_2O$ (Strem Chemicals, 99.9% Au), which contained the calculated amounts of the Zn and Au salts required to give the desired Au loading on ZnO, was heated to 80 °C. Na_2CO_3 solution (1 mol l^{-1}) was then added, with continuous stirring, until pH 9 was reached. The precipitate was then aged for 20 min prior to vacuum filtration, washed with hot deionised H_2O (1 l), dried overnight at 110 °C and calcined at 400 °C for 4 h.

A ZnO supported catalyst containing 5 wt.% Au metal was prepared by impregnation. The required amount of ZnO support material was added to a solution containing a calculated amount of $HAuCl_4$ to give a 5 wt.% loading of Au^0. The mixture was allowed to dry by evaporation to a thick paste at 80 °C (*ca.* 5 h) with continuous stirring, dried at 110 °C for 16 h and then calcined at 300 °C for 4 h. The ZnO sample was prepared by precipitation of a basic carbonate by the reaction of zinc nitrate with sodium carbonate, followed by drying and calcination at 400 °C for 4 h. Prior to use, catalyst samples were pelleted and sieved to give agglomerates 0.6–1.0 mm in diameter. Following this, they were reduced *in situ* in flowing H_2 (60 ml min^{-1}) by heating from ambient temperature to the required reduction temperature at a rate of 5 °C min^{-1} and then maintaining that temperature for 1 h. The reaction was then started or thiophene modification was performed prior to reaction.

Catalyst characterisation

X-ray powder diffraction. X-ray diffraction data was obtained using an Enraf Nonius FR590 diffractometer working at 40 kV and 30 mA using Cu-Kα radiation. This instrument was equipped with a static detector with a measuring arc of 120°.

Infrared spectroscopy. Compressed self-supporting discs of calcined catalyst precursor were mounted in a vacuum infrared cell fitted with fluorite optical window and were then reduced within the cell. Spectra were recorded at 4 cm^{-1} resolution using a Perkin Elmer Spectrum 2000 Fourier Transform Infra-red Spectrometer. Unless otherwise stated, discs were at ambient temperature in the spectrometer beam (*ca.* 25 °C) during the adsorption and desorption of CO and while spectra were recorded.

Transmission electron microscopy. Samples suitable for transmission electron microscopy analysis were prepared by dispersing the catalyst powder onto a lacy carbon film supported on a copper mesh grid. Transmission electron microscopy observations were made in a JEOL 2000 EX high resolution electron microscope operating at 200 kV. Chemical microanalysis was performed in a VG HB601 STEM operating at 100 kV with a 1 nm probe size, equipped with an Oxford Instruments.Link EDX analysis system (RTS/FLSZ).

Catalyst testing

Reactions were carried out in a continuous flow, fixed-bed, micro-reactor (9 mm i.d.) at atmospheric pressure using on-line GC analysis (Varian 3400 GC, equipped with an FID and DBwax megabore column, 0.53 mm × 30 m) for separation and analysis of the reactant and products. The catalyst (200 mg) was reduced *in situ* in a flow of hydrogen (60 ml min^{-1}) at a specific temperature for 1 h prior to reaction. But-2-enal was fed into the system by means of a calibrated syringe pump into a flow of hydrogen (weight hourly space velocity = 0.7 h^{-1} and H_2 : but-2-enal ratio = 14 : 1). Modification of the catalyst was achieved *via* direct injection of either 0.5 or 1 μl of thiophene into a flow of hydrogen with the catalyst sample maintained at 250 °C after reduction. The reaction was started either immediately after reduction and cooling, if necessary, to the reaction temperature or 15 min after injection of thiophene.

Results and discussion

Effect of [Au] on catalyst performance of Au/ZnO

In our earlier communication[24] we showed that 5 wt.% Au supported on ZnO or ZrO_2 was active for the hydrogenation of but-2-enal and that, for catalysts prepared using coprecipitation, high selectivities could be observed for the unsaturated alcohol, but-2-en-1-ol. However, the 5 wt.% Au/ZnO catalyst was more active and selective than the 5 wt.% ZrO_2 catalyst. In view of this, the hydrogenation of but-2-enal was investigated over Au/ZnO catalysts containing 1, 2, 5 and 10 wt.% Au prepared by coprecipitation and the results are given in Table 1. For all the catalysts, conversion tends to decrease with increasing time-on-stream. However, the steady state conversion attained after *ca.* 60 min, generally increases with increasing [Au] with the best results being achieved with the 5 wt.% catalyst. In addition, the selectivity to the unsaturated alcohol but-2-en-l-ol also increased with time-on-stream for all catalysts and the highest selectivity was observed for 1 wt.% Au. However, the yield of but-2-en-1-ol at steady state was observed to be 3.9, 6.4, 7.2 and 7.1×10^{-4} mol g $catalysts^{-1}$ h^{-1} for the 1, 2, 5 and 10 wt.% catalysts respectively. This indicates that, for the selective hydrogenation of the C=O group in but-2-enal, catalysts containing higher concentrations of Au give the best results. By-product formation is also increased with increasing Au concentration and, in particular, for 10 wt.% Au/ZuO the formation of total hydrogenation and hydrogenolysis products becomes quite marked. In view of this catalysts containing 5 wt.% Au give a reasonable compromise between enhanced formation of the unsaturated alcohol and reduced by-product formation. In contrast, a 5 wt.% Au/ZnO catalyst prepared by impregnation, and subjected to the same reduction and reactions conditions as the co-precipitated catalyst, was found to be totally inactive for this hydrogenation reaction.

The effect of reaction temperature on the hydrogenation of but-2-enal was investigated for 2 and 5 wt.% Au/ZnO catalysts and the results are given in Table 1. Again the conversion of but-2-enal was found to decrease with time-on-stream at the lower temperature of 150 °C as was observed at 250 °C and, as expected, the steady conversion increases with increasing temperature. The selectivity to but-2-en-1-ol increases with time-on-stream and higher selectivities are observed at 250 °C than at 150 °C.

Effect of reduction temperature on catalyst performance of 5 wt.% Au/ZnO

The hydrogenation of but-2-enal was investigated over 5 wt.% Au/ZnO that had been reduced at 250–400 °C prior to reaction and the results are given in Table 2. The conversion decreases with increasing time-on-stream for all catalysts, but at steady state the highest conversion was observed with catalysts reduced at 300 °C. In general, the selectivity to the unsaturated alcohol, but-2-en-1-ol increased with increasing reduction temperature and, for the catalyst reduced at 400 °C, *ca.* 80% selectivity to but-2-en-1-ol was observed. The formation of by-products from dimerisation, total hydrogenation and hydrogenolysis also decreased with increasing reduction temperature which accounts, in part, for the improved selectivity to the selective hydrogenation product. It should be noted that, in previous studies for the hydrogenation of but-2-enal, which have recently been reviewed by Claus,[28] the highest selectivities for but-2-en-l-ol are in the range 60–70%, at conversions comparable to those observed in this study. In

Table 1 Effect of Au loading on the performance of Au/ZnO catalysts for but-2-enal hydrogenation

[Au] (wt.%)	Reaction temp./°C	Time/ min	Conversion (%)	Selectivity (%)[a]					
				B–AL	B=OL	B–OL	2EH	2E2H	Others
1[b]	250	10	7.2	45.1	41.5	—	—	—	13.4
		30	4.4	36.8	57.7	—	—	—	5.5
		60	3.5	39.1	60.9	—	—	—	—
		120	3.3	37.6	62.4	—	—	—	—
		180	2.4	39.9	60.1	—	—	—	—
2[c]	150	10	7.3	50	25	6.3	16.6	—	2.2
		20	2.9	63.2	35.4	—	—	—	1.6
		30	2.2	65.4	32.8	—	—	—	1.8
		40	1.4	75.1	20.5	—	—	—	4.4
		60	1.3	68.8	26.1	—	—	—	5.2
2[b]	250	10	6.7	81.8	2.3	8.1	1.5	1.6	4.7
		20	8.3	86.2	7.3	2.5	—	—	3.9
		30	4.7	82.3	15.0	—	—	—	2.7
		45	4.8	71.0	26.8	—	—	—	2.2
		60	5.6	72.8	24.9	—	—	—	2.3
		105	5.2	65.8	32.2	—	—	—	1.9
		120	4.9	56.3	42.2	—	—	—	1.5
		180	6.7	56.0	42.5	—	—	—	1.5
5[c]	150	10	6.0	20.8	44.4	33.7	—	—	1.2
		20	2.5	32.6	61.3	2.5	—	—	3.9
		30	0.8	37.9	54.7	—	—	—	7.4
		60	1.0	49.5	48.1	—	—	—	2.4
		125	0.4	56.7	43.3	—	—	—	—
		180	0.2	67.2	32.8	—	—	—	—
5[b]	250	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
		120	7.6	35.9	51.0	—	—	1.1	12.0
		180	7.8	34.1	54.1	—	—	1.1	10.7
10[b]	250	10	11.9	38.2	21.3	11.5	—	—	29.0
		30	7.4	40.2	45.4	—	—	—	14.4
		60	8.3	41.2	45.6	—	—	—	13.2
		120	8.1	39.0	46.6	—	—	—	14.4
		150	10.6	39.0	46.4	—	—	—	14.6

[a] B–Al: butanal, B=OL: but-2-en-1-ol, B–OL: butan-1-ol, 2EH: 2-ethyl hexanal, 2E2H: 2-ethyl-2-hexanal, others: butane and C_3 molecules. [b] Catalyst reduced at 250 °C prior to reaction at 250 °C. [c] Catalyst reduced at 150 °C prior to reaction at 150 °C.

Table 2 Effect of reduction temperature on the performance of 5 wt.% Au/ZnO for but-2-enal hydrogenation at 250 °C

Reduction[a] temperature /°C	Time /min	Conversion (%)	Product selectivity (%)[b]					
			B–AL	B=OL	B–OL	2EH	2E2H	Others
250	20	13.1	32.5	50.2	—	2.8	1.4	13.1
	30	8.7	37.8	47.8	—	—	0.9	13.5
	60	8.9	35.1	51.7	—	—	—	13.2
	120	7.6	35.9	51.0	—	—	1.1	12.0
	180	7.8	34.1	54.1	—	—	1.1	10.7
300	20	13	28.6	60.1	—	—	—	11.3
	30	12.3	27.7	57.1	—	4.5	—	10.7
	60	10.8	27.9	56.0	—	5.1	—	11.0
	130	13.5	25.0	63.9	—	2.4	—	8.7
	180	11.8	25.2	62.9	—	2.4	—	9.5
350	20	6.7	26.1	63.8	—	—	—	10.1
	30	3.4	29.5	57.7	—	—	—	12.8
	70	4.5	28.4	61.2	—	—	—	10.4
	120	4.4	28.6	60.8	—	—	—	10.6
	195	3.7	30.6	57.5	—	—	—	11.9
400	20	6.1	18.9	76.5	—	—	—	4.6
	30	7.7	16.4	80.2	—	—	—	3.4
	60	6.3	17.4	79.2	—	—	—	3.4
	120	4.7	17.6	79.6	—	—	—	2.8
	185	5.3	16.1	80.7	—	—	—	3.2

[a] Catalysts calcined at 400 °C, 4 h; treated with H_2 from ambient temperature to the specified reduction temperature prior to cooling to the reaction temperature of 250 °C. [b] B–AL: butanal, B=OL: but-2-en-1-ol. B–OL: butan-1-ol, 2EH: 2-ethyl hexanal, 2E2H: 2-ethyl-2-hexenal, others: butane and C_3 molecules.

view of this, the 80% selectivities observed in this study represent a significant improvement.

Effect of thiophene pre-treatment on Au/ZnO catalysts

In our previous communication, we showed that thiophene modification of Au/ZnO and Au/ZrO_2 catalysts could enhance the selectivity and yield of but-2-en-l-ol. The effect was maintained as the catalyst deactivated with increased time-on-line. We have now investigated the hydrogenation of but-2-enal over 5 wt.% Au/ZnO that had been reduced at 250 °C and pretreated with 0, 0.5 and 1.0 μl thiophene, representing 0, 8.2×10^{-5} and 1.64×10^{-4} (mol S) $(\text{mol Au})^{-1}$ respectively, and the results are shown in Fig. 1. Pre-treatment with thiophene had a marked effect on the initial conversion observed at 10 min time-on-steam, with thiophene pre-treated catalysts given lower conversion. However, the effect was less pronounced when steady state conversion had been attained.

For the catalyst treated with 0.5 μl thiophene prior to reaction, the yield of the unsaturated alcohol but-2-en-l-ol was significantly enhanced when steady state conversion had been attained, compared with both the untreated and the 1.0 μl thiophene-treated catalysts. This indicates that the effect is sensitive to the concentration of thiophene, which has previously been observed with thiophene modification of Cu/γ-Al_2O_3 catalysts for the same reaction.[25–27]

The effect of thiophene pre-treatment was further investigated using 2 and 5 wt.% Au/ZnO catalysts pre-treated with 0.5 μl thiophene and the results are given in Table 3. At both 150 and 250 °C, thiophene pre-treatment leads to a lower conversion being observed (compared data in Table 3 with that in Table 1). For all the catalysts, thiophene pre-treatment leads to an increase in selectivity to the unsaturated alcohol but-2-en-l-ol, the effect being most pronounced for 2 wt.% Au/ZnO at 150 °C. However, in this case, the yield of but-2-en-l-ol remains similar for both untreated and treated catalysts at steady state conversion. By way of contrast, thiophene pretreatment of the 5 wt.% Au/ZnO catalyst, leads to an increase in the rate of formation of but-2-en-ol (Fig. 2). Hence the effect of thiophene pre-treatment is also sensitive to the concentration of Au present in the material.

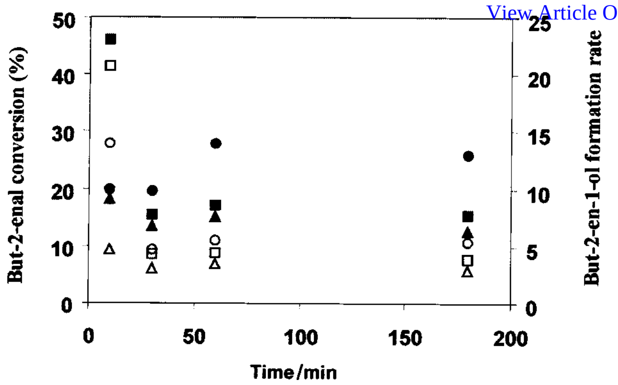

Fig. 1 Effect of thiophene-modification on but-2-enal conversion and the yield of but-2-en-1-ol over 5 wt.% Au/ZnO. Key: (□) 0 μl thiophene; (○) 0.5 μl thiophene; (△) 1.0 μl thiophene. Open symbols: but-2-enal conversion (%); closed symbols: rate of but-2-en-1-ol formation (10^{-4} mol g^{-1} h^{-1}).

The effect of thiophene pre-treatment on a 5 wt.% Au/ZnO catalyst that had been reduced at 400 °C was investigated and the results are also given in Table 3. Comparison with the results for the untreated catalyst (Table 2) shows that thiophene pre-treatment of this catalyst does not have a significant effect, in contrast with the result for the same catalyst reduced at 250 °C (Fig. 2).

Table 3 Effect of reaction temperature on thiophene-pretreated catalysts on the hydrogenation of but-2-enal

[Au] (wt.%)	Reaction temperature /°C	Time /min	Conversion (%)	Product selectivity (%)[a]					
				B–AL	B=OL	B–OL	2EH	2E2H	Other
2-S[b]	150	10	4.8	48.9	46.2	—	—	—	5
		20	1.3	37.9	56.9	—	—	—	5.2
		30	1.2	29.9	64.1	—	—	—	6
		40	0.7	34.2	55.4	—	—	—	10.4
		50	0.5	31.4	58.4	—	—	—	10.2
2-S[c]	250	10	5.0	75.2	16.9	0.9	0.4	—	6.5
		25	5.4	66.4	29.7	—	—	—	3.9
		40	4.6	59.9	36.0	—	0.9	—	3.2
		60	3.8	58.7	38.6	—	—	—	2.8
		120	3.1	52.8	44.6	—	—	—	2.7
		150	3.0	55.0	42.3	—	—	—	2.7
5-S[b]	150	10	5.8	25.1	65.4	7.0	—	—	2.5
		20	2.4	27.2	71.5	—	—	—	2.4
		30	2.0	31.7	66.2	—	—	—	2.1
		60	1.0	42.1	53.7	—	—	—	—
		120	0.5	48.6	51.4	—	—	—	—
		180	0.2	66.9	33.1	—	—	—	—
5-S[c]	250	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	65.6	—	—	—	7.8
5-S[d]	250	10	4.8	29.4	55.1	—	3.6	—	11.9
		20	5.6	16.9	80.3	—	tr	—	2.8
		30	4.9	15.8	81.3	—	tr	—	2.1
		60	4.8	16.4	81.1	—	—	—	2.5
		90	4.8	15.2	83.3	—	—	—	1.6
		170	5.5	13.3	85.1	—	—	—	1.6
		180	6.1	11.9	86.9	—	—	—	1.2

[a] B–AL: butanol; B=OL: but-2-en-1-ol; B–OL: butan-1-ol; 2EH: 2-ethylhexanal; 2E2H: 2-ethyl-2-hexenal; other: butane and C_3 products. [b] Catalyst reduced at 150 °C, and treated with 0.5 μl thiophene. [c] Catalyst reduced at 250 °C and treated with 0.5 μl thiophene. [d] Catalyst reduced at 400 °C, treated with 0.5 μl thiophene and cooled to 250 °C for reaction.

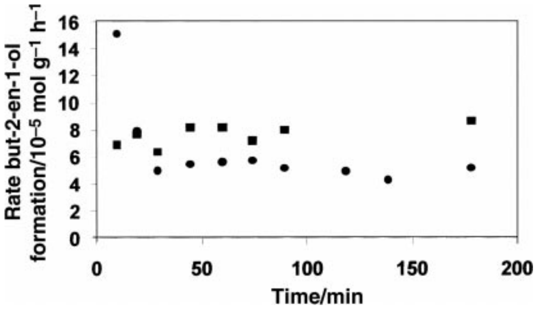

Fig. 2 Effect of thiophene-modification on the rate of but-2-en-1-ol formation over 5 wt.% Au/ZnO at 250 °C. (●) Au/ZnO; (■) thiophene-modified Au/ZnO.

Characterisation of supported Au catalysts

Powder X-ray diffraction. The powder X-ray diffraction patterns of Au/ZnO samples prepared by coprecipitation as a function of Au content are shown in Fig. 3. Reflections due to Au crystallites were observed only with the highest loading, 10 wt.% Au/ZnO (Fig. 5(e) below). However, the reflections due to ZnO broadened with increasing Au content indicating smaller ZnO crystallites were present. Using the Scherrer equation, the calculated ZnO particle size decreased from >10 nm for 0.25 wt.% Au/ZnO to 8.5 nm for 10 wt.% Au/ZnO.

Infrared spectroscopy. Similar spectroscopic characteristics were observed for the adsorption of thiophene on reduced ZnO and Au/ZnO. Hydrogen bonding interactions between weakly adsorbed thiophene molecules and surface hydroxy groups on ZnO led to decreases in adsorption intensity at 3680, 3618, 3540 and 3440 cm^{-1}. These were observed on a broad group band envelope due to vibrations of hydroxy groups which were perturbed by thiophene. Bands due to hydroxy groups on ZnO have previously been reported to exist at 3670, 3620, 3550 and 3440 cm^{-1}.[29] Desorption of thiophene from ZnO or Au/ZnO by evacuation at 25 °C was apparently complete after 30 min, there being no detectable evidence for residual thiophene or surface products of chemisorption. The hydroxy groups were effectively restored to their initial state before exposure to thiophene by this simple evacuation treatment.

Admission of CO to Au/ZnO at low pressure gave a band at 2035 cm^{-1} with a shoulder at *ca.* 2045 cm^{-1}. These two bands became indistinguishable at higher coverages with a combined maximum at 2045 cm^{-1} (Fig. 4A). Adsorbed CO molecules giving rise to these bands were resistant to desorption by evacuation at 25 °C. Exposure of 5 wt.% Au/ZnO to thiophene at 250 °C (the temperature of modification used in catalysis experiments), followed by evacuation at 25 °C and admission of CO, gave bands at 2108 and 2043 cm^{-1} (Fig. 4B). The former band disappeared and the latter band grew and shifted to 2058 cm^{-1} with increasing CO pressure (Fig. 4B). Furthermore, a weak band also appeared at 2015 cm^{-1} with increasing CO pressure. Evacuation of the sample at 298 K for 30 min was observed to reduced the 2058 cm^{-1} band intensity by 65%.

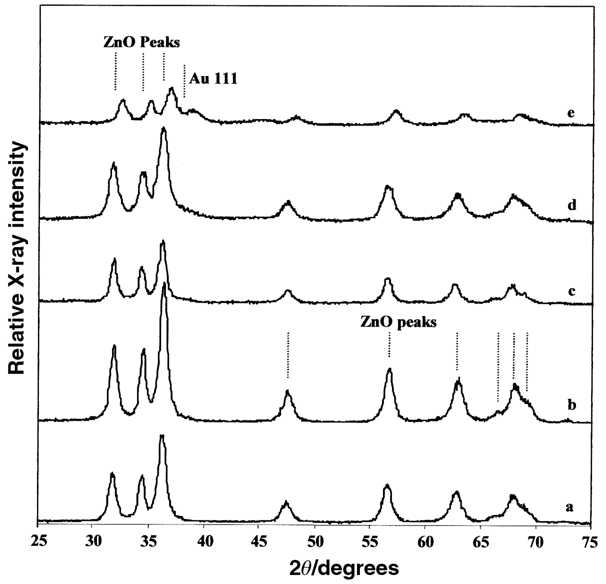

Fig. 3 Powder X-ray diffraction patterns of Au/ZnO catalysts prepared by coprecipitation. (a) 0.25 wt.% Au, (b) 0.5 wt.% Au, (c) 1 wt.% Au, (d) 5 wt.% Au (e) 10 wt.% Au.

The observed bands at 2040–2055 cm^{-1} are at unusually low wavenumbers for CO adsorbed on Au,[1] although bands at 2060 and 2040 cm^{-1} have previously been reported for Au/SiO$_2$ and Au/MgO respectively, which had been reduced in H$_2$ at 350 °C.[30] In earlier studies, a band at 2070–2080 cm^{-1} for Au/SiO reduced at 375 °C has been attributed to CO adsorption on large Au particles.[32] A band observed at 2038 cm^{-1} for Au/TiO$_2$ was not assigned in the study by Bollinger and Vannice.[33] The proposed explanation of the bands at 2040–2055 cm^{-1} was that they were due to CO on Au^0 terraces. However, there is a problem with this interpretation in that 5 wt.% Au/ZnO material only gave bands around 2045 cm^{-1}, even though the Au particle sizes present would demand the existence of a significant proportion of incompletely coordinated edge sites.[34] Bands in this region might also be attributed to ν_{sym} vibrations of gem-dicarbonyl species which, for Au(CO)$_2$, are known to give a band at 2072 cm^{-1}.[35] This assignment has been rejected for Au/TiO$_2$ because of the complete absence of a band below 2000 cm^{-1} due to ν_{asym} vibrations which give a band at 1936 cm^{-1} for Au(CO)$_2$.[36] This band is also absent from the spectra of Au/ZnO catalysts. However, the absence of this band could be explained of the metal–surface selection rule,[37] requiring that only vibrations giving dipole changes perpendicular to the surface were infrared active, was operating. A shoulder at 1950 cm^{-1} has been observed for Au/MgO but was assigned to bridging or multi-bounded CO.[30] The assignment of at least a component of the bands at 2040–2055 cm^{-1} to gem-dicarbonyl species at incompletely coordinated Au sites would be consistent with the expected population of edge sites[34] on 2–4 nm particles. However, the absence of a band at 1900–2000 cm^{-1} does not allow this assignment to be confirmed and, therefore, assignment to linear CO still remains a plausible alternative.

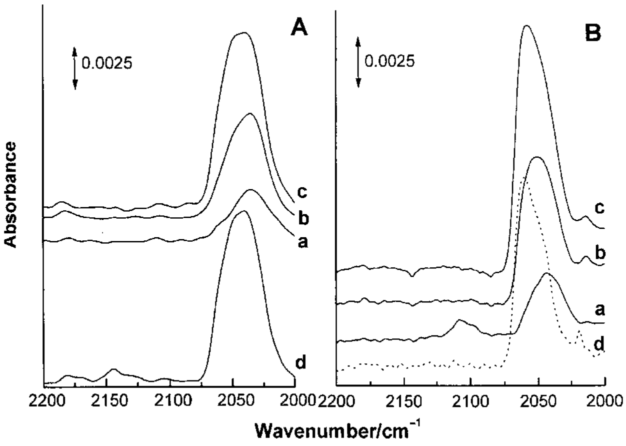

Fig. 4 FTIR spectra of 5 wt.% Au/ZnO reduced at 250 °C and (A) exposed to CO at (a) 2, (b) 6 and (c) 10 mm Hg and (d) evacuated for 30 min. (B) exposed to thiophene (2 mm Hg) at 250 °C, evacuated at 25 °C and exposed to CO at (a) 2, (b) 6 and (c) 10 mm Hg and (d) evacuated for 30 min.

The modification of 5 wt.% AU/ZnO with thiophene at 250 °C (Fig. 4B) gave thiophene decomposition products on the Au Surface which resulted in shifts of 8–13 cm^{-1} to higher wavenumbers for subsequently adsorbed CO. These products could not be detected and, therefore, identified from spectra of adsorbed thiophene alone. However, the thiophene modification hardly affected the number of available sites for CO adsorption, but nevertheless, had an effect on *all* the sites in the sense of strengthening the C–O bond in the adsorbed CO. Electron transfer from metal surfaces to adsorbed sulfur species have been reported previously.[27,38,39]

Transmission electron microscopy. Samples of 2, 5 and 10 wt.% Au/ZnO prepared by coprecipitation, were examined by transmission electron microscopy (Fig. 5). The 2 wt.% Au/ZnO (Fig. 5(a)) showed the presence of 2–4 nm diameter Au nanoparticles typically exhibiting cub-octahedral or isohedral morphology, as well as some even smaller particles. The ZnO support particles, for all samples, were highly crystalline with 15–20 nm diameter. The 5 wt.% Au/ZnO sample (Fig. 5(b)) exhibited a very narrow size distribution of Au particles with diameters of 4–5 nm, which were homogeneously distributed over the support. The Au particles were well faceted, untwinned, single crystals having a truncated cub-octahedral morphology. The 10 wt.% Au/ZnO material (Fig. 5(c)) also showed the presence of a good dispersion of discrete Au particles, but notably a bimodal size distribution was apparent. Larger particles with diameters in the range 6–10 nm were commonly observed along with others that were much smaller in size, typically 1–3 nm.

The effect of thiophene pre-treatment and reaction with but-2-enal was investigated and typical micrographs for 2 wt.% Au/ZnO are given in Fig. 5(d) and (e). The unused calcined sample that had been reduced in hydrogen at 150 °C showed the presence of cub-octahedral particles of Au, that are typically 2.5 nm in size (Fig. 5(a)). Pre-treatment with 0.5 μl thiophene did not markedly affect the Au particle size, morphology, or distribution (Fig. 5(d)). Following reaction for the hydrogenation of but-2-enal at 150 °C, the catalyst again showed the presence of small, clean Au particles (Fig. 5(e)) suggesting that, under these reaction conditions, the Au particle size is not affected significantly by the hydrogenation reaction.

The effect of reduction temperature on the 5 wt.% Au/ZnO was also systematically examined by electron microscopy, as shown in Fig. 6. The unreduced sample (Fig. 6(a)) showed the

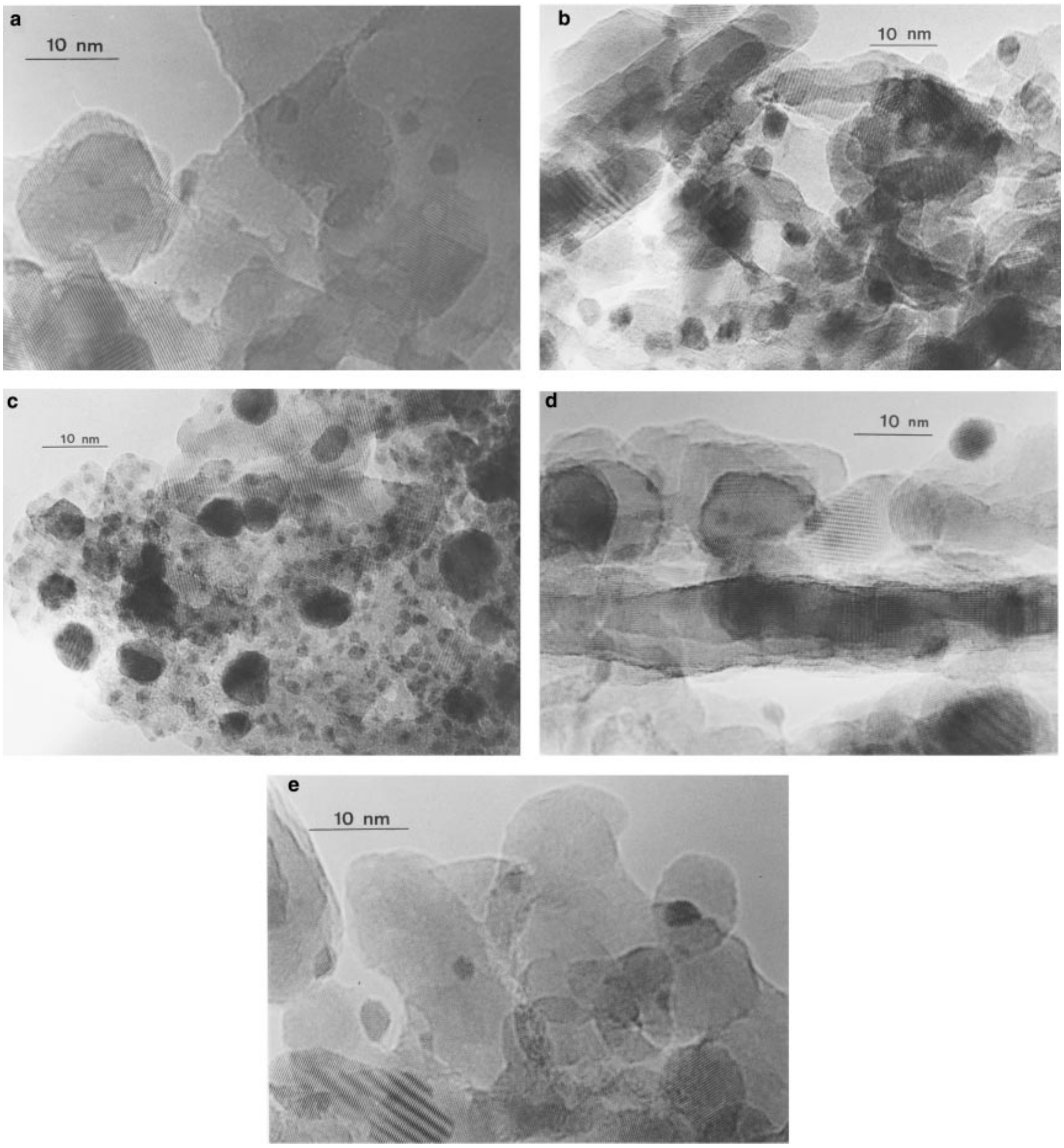

Fig. 5 Transmission electron micrographs for Au/ZnO catalysts with different metal loadings. The fresh calcined catalysts are (a) 2 wt.% Au, (b) 5 wt.% Au, (c) 10 wt.% Au. Image (d) shows the 2 wt.% Au/ZnO catalyst modified by thiophene, (e) shows 2 wt.% Au/ZnO unmodified following reaction at 150 °C.

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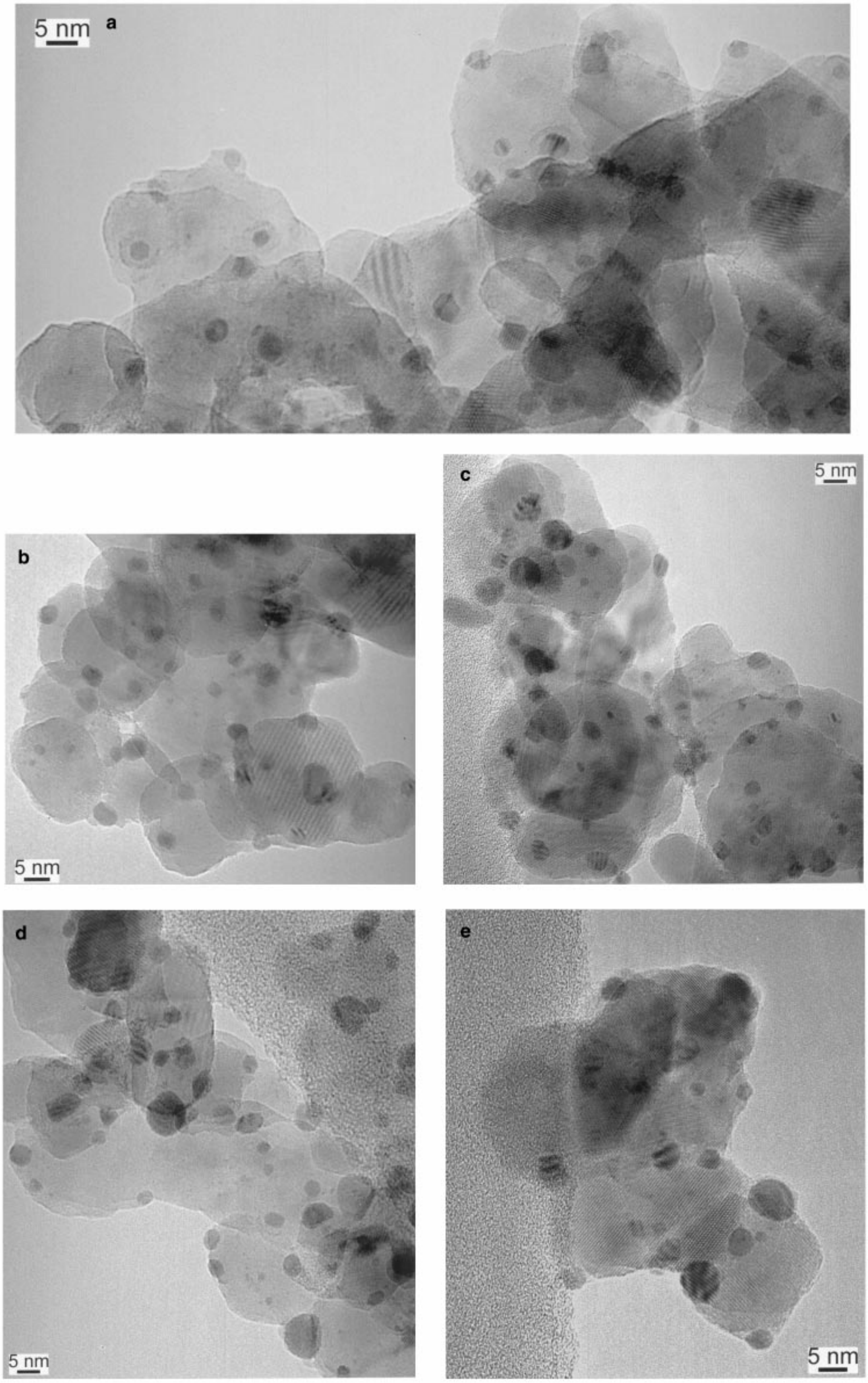

Fig. 6 Transmission electron micrographs of fresh calcined 5 wt.% Au/ZnO catalysts. (a) is the unreduced material, whereas the others are reduced at (b) 250, (c) 300, (d) 350 and (e) 400 °C respectively.

presence of a uniform dispersion of 4 nm diameter Au particles. These particles were epitaxial with the substrate oxide and preferentially expose {111} and {100} surface facets that are characteristic of a cub-octahedral morphology. In many cases, there is evidence of a thin disordered surface coating of unknown composition on the Au particles. The sample reduced at 250 °C (Fig. 6(b)) showed the presence of a homogeneous distribution of Au nanoparticles with {111} and {100} surface facets again evident. Most particles were still typically ~4 nm in diameter but a significant number had grown to around 6 nm. There was no evidence of a surface overlayer on any of the Au particles and, in this case, the particle–substrate epitaxy is less convincing. In addition, there is some evidence of sub-nanometric 'fleck'-type contrast on the ZnO support. STEM-energy dispersive X-ray (EDX) analysis has been used to identify the origin of this contrast. Fig. 7 shows these EDX spectra. The existence of weak signals at ~2.1 and 8 eV from the area of the 'fleck' is clear evidence that the contrast originates from a very small Au particle or raft on the ZnO support. The sample reduced at 300 °C (Fig. 6(c)) has a much larger size distribution of Au particles, typically ranging in diameter from 3–8 nm. There are also a considerable number of sub-1 nm diameter 'fleck'-type Au particles present. Furthermore, there is little evidence of any

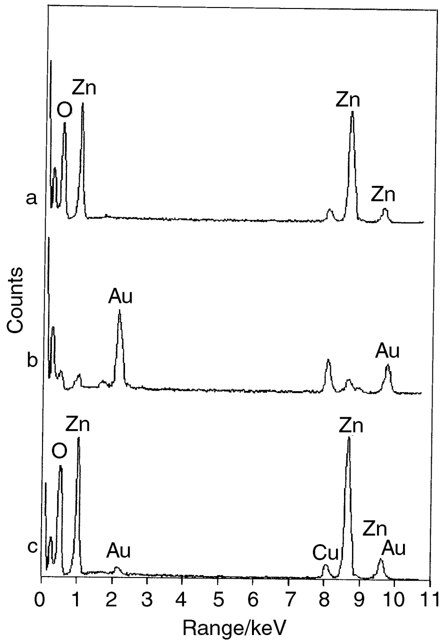

Fig. 7 Energy disperse X-ray spectra taken from various regions in the 5 wt.% Au/ZnO catalyst. These were obtained with a 1 nm probe positioned on (a) a region of clean ZnO support, (b) a 4 nm Au particle seen in profile and (c) a region showing nm scale 'fleck'-like contrast on the ZnO support.

epitaxial relationship between the Au particles and the support oxide in this sample. The sample reduced at 350 °C (Fig. 6(d)) shows evidence of considerable sintering of the Au, since particles 10–15 nm in diameter are not uncommon. Many of the larger particles show multiple twinning. However, Au particles in the range 4–6 nm in diameter are still evident, as are the 'fleck'-like sub-nanometric Au rafts. The sample subjected to the highest reduction temperature of 400 °C (Fig. 6(e)), showed even more evidence for Au sintering and particles up to 20 nm in diameter have been observed. Consequently, a much smaller fraction of the Au particles are now in the 4–6 nm and 1–3 nm size ranges. Significantly, there is still some occasional evidence of the presence of sub-nm Au particles *via* the 'fleck'-type contrast on the ZnO supports.

Hence, from this detailed transmission electron microscopy study, it is apparent that, as the reduction temperature is increased from 250 to 400 °C, there is a significant effect on the Au particle size distribution. As the reduction temperature is increased, the 4–5 nm Au particles, characteristic of the unreduced material, are transferred to give Au particles with both larger and smaller diameters, *i.e.* creating an effective approximate bimodal distribution.

Comments on the nature of the active site for selective hydrogenation of but-2-enal to but-2-en-1-ol

There are two effects that require further comment, namely (a) the effect of Au particle size on hydrogenation selectivity and (b) the effect of thiophene modification. The results of the present study indicate that, as both the Au loading and catalyst reduction temperature are increased, the selectivity for the formation of the unsaturated alcohol is enhanced. In addition, thiophene modification of catalysts reduced at 400 °C has no significant effect and there is no further enhancement in the yield of the unsaturated alcohols, whereas for catalysts reduced at 250 °C, there is a pronounced enhancement in the yield of unsaturated alcohol upon thiophene modification. The transmission electron microscopy studies indicate that, as the Au concentrations and catalyst reduction temperatures are increased, the Au particle size also generally increases. However, for the sample containing the highest [Au] investigated (10 wt.% Au/ZnO), there is a clear bimodal distribution for the Au nanoparticles, with particles of 1–3 nm and 6–10 nm being present. In addition, as the reduction temperature was increased from 250 to 400 °C, it was apparent that this induced a bimodal distribution in the Au nanoparticles. The relative proportion of particles in the range 4–5 nm decreased with increasing reduction temperature giving a concomitant increase in the proportions of smaller and larger particles. If we consider the catalytic results of these two sets of samples together, we note that the sample containing low Au concentrations (1.2 wt.% Au) also contain small particles similar to those observed in the 10 wt.% Au/ZnO sample and the 5 wt.% Au/ZnO sample reduced at higher temperatures. In view of this fact, we do not consider that the small Au nanoparticles (diameter <2 nm) are associated with the high selectivities to but-2-en-1-ol observed, in the absence of thiophene modification, with the high [Au] and high reduction temperature catalysts. Hence, we propose that the active sites for selective hydrogenation of but-2-enal to but-2-en-1-ol are associated with the presence of large Au particles. This is in contrast to the active site in supported Au catalysts used for the oxidation of CO under ambient conditions. For this latter reaction, it is generally agreed that the most active catalysts comprise 2–5 nm Au particles and that it is the periphery between the Au particle and the support that provides the active site for CO activation under mild conditions. Larger Au particles are inactive for CO activation, whereas we consider that these are both active and selective for the selective hydrogenation of α,β-unsaturated aldehydes.

In contrast, the effect of thiophene is most marked for the catalysts with relatively low [Au] (<5 wt.% Au) or prepared using low reduction temperatures which contain a vast majority of Au nanoparticles with diameters typically in the 2–5 nm range. In effect, this provides evidence in support of the proposal that large Au particles are the origin of the enhanced selectivity to but-2-en-1-ol. The samples giving the highest selectivity to but-2-en-1-ol (*i.e.* 5 wt.% Au/ZnO reduced at 400 °C) still contain an appreciable concentration of small Au-nanoparticles, but the thiophene treatment has a very limited effect on the selectivity to but-2-en-1-ol. If the small Au particles were the origin of the high selectivity, it could reasonably be expected that this would have been enhanced further on thiophene addition. As this is not observed, it can be concluded that the effect is associated with the larger Au particles. Transmission electron microscopy has shown that thiophene modification does not affect the Au particle size and so the origin of the effect of thiophene modification is not expected to be morphological in nature. It is clear that thiophene modification leads to a *promotion* in the rate of formation of but-2-en-1-ol from the hydrogenation of but-2-enal for supported Au catalysts. Furthermore, infrared spectroscopy studies indicate that thiophene undergoes irreversible dissociative adsorption giving a surface on which the Au sites are still available for CO adsorption, and that the effect of the sulfur is to act as an electronic promoter as observed for Cu catalysts previously.[27–29] It is possible that this is a general effect for this triad of metals and results for Ag/ZnO catalysts will be reported elsewhere.[40]

Acknowledgements

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