

# Effect of thiophene modification on supported metal catalysts for the hydrogenation of but-2-enal

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## Abstract

In contrast to the behaviour of supported Cu and Au catalysts, the selectivity of but-2-en-1-ol in the gas-phase hydrogenation of but-2-enal at 120 °C is not increased by pre-treatment of Co/Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub>, Co/ZnO, Ni/Al<sub>2</sub>O<sub>3</sub>, Ru/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> with thiophene. Selectivities to by-products formed by dimerisation and hydrogenolysis are, however, decreased. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* But-2-enal; Thiophene; Hydrogenation

## 1. Introduction

The control of selectivity in heterogeneously catalysed reactions remains an area of intense research activity. In particular, the selective hydrogenation of substrates that contain a range of unsaturated functional groups is an important process in the manufacture of fine chemicals. A specific example concerns the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes over heterogeneous transition metal catalysts. This tends to give saturated aldehydes and alcohols as the dominant products. In recent years, a significant amount of fundamental research has addressed the design of catalysts for the selective synthesis of the unsaturated allylic alcohols in this reaction. Selectivity control [1–16] in this reaction is influenced by many factors, including the nature of the support [4,5], metal particle size [5,6] and the introduction of additives [6–12] and much of this research has been recently reviewed

by Claus [1]. With respect to additives, Pt catalysts have been shown to exhibit enhanced selectivity to the unsaturated alcohol when oxides of Ge, Ga and Sn were added [7–9], and this effect may be related to site blocking on the surface of the metal crystallites, which is observed for similar catalysts used in selective oxidation [17].

We have previously demonstrated [13–15] that partial poisoning of supported copper catalysts using sulphur can be a viable approach for the design of selective catalysts. Indeed, the modification of Cu/Al<sub>2</sub>O<sub>3</sub> by very low levels of thiophene significantly enhanced the selectivity of the formation of but-2-en-1-ol from the hydrogenation of but-2-enal. Detailed analyses of these results [13] showed that sulphur acted as a promoter for this selective hydrogenation reaction, rather than a poison as would have been expected based on the known effects of sulphur compounds on hydrogenation catalysts. Most recently [18], we have shown that similar effects are observed with Au/ZnO.

The present study of but-2-enal hydrogenation was aimed at testing whether the beneficial effects of

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thiophene modification of Cu/Al<sub>2</sub>O<sub>3</sub> and Au/ZnO catalysts could also be observed for supported transition metal catalysts.

## 2. Experimental

Co/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> and Co/SiO<sub>2</sub> each with 5 wt.% metal were prepared by addition of alumina (Condea SCF, Puralex ScFa, surface area 140 m<sup>2</sup> g<sup>-1</sup>) or silica (Cab-O-Sil M5, 200 m<sup>2</sup> g<sup>-1</sup>) to an aqueous solution of the metal nitrate. In addition, a Co/ZnO sample was prepared by impregnation of ZnO with cobalt nitrate. After evaporation to dryness at 80 °C, the resulting solid was dried (110 °C, 16 h) prior to calcination (400 °C, 3 h). Rh/Al<sub>2</sub>O<sub>3</sub> (5 wt.%) and Ru/Al<sub>2</sub>O<sub>3</sub> were obtained from Aldrich and the 5 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was obtained from Johnson Matthey.

For the catalytic studies, the calcined materials were pelleted and sieved to give particles of 0.6–1.0 mm in diameter. The vapour-phase hydrogenation of but-2-enal was conducted in a continuous flow fixed-bed reactor at atmospheric pressure. The catalyst (0.1 g) was loaded to a Pyrex reactor tube (9 mm i.d.) and supported on a glass frit. The samples were then reduced for 2 h in situ in a flow of pure H<sub>2</sub> (60 ml min<sup>-1</sup>) at 400 °C before cooling to 120 °C for reaction. The H<sub>2</sub> flow at 1 atm pressure was adjusted to 10 ml min<sup>-1</sup> and liquid but-2-enal was introduced at a controlled flow rate by means of a calibrated syringe pump and was vaporised in the H<sub>2</sub> flow. The H<sub>2</sub>:but-2-enal molar ratio was 14:1 (WHSV = 1.3 h<sup>-1</sup>). Catalyst modification involved the direct injection of thiophene (1.0 μl) into the catalyst after reduction and cooling to 200 °C, prior to cooling to the reduction temperature. Previous characterisation [15,19] studies using infra-red spectroscopy have shown that the thiophene is dissociatively adsorbed under these conditions to give adsorbed sulphur. Analysis of the reactant and products was determined using on-line gas chromatography.

## 3. Results and discussion

The hydrogenation of but-2-enal over unmodified Co/Al<sub>2</sub>O<sub>3</sub> showed a steady decrease in catalyst activity with time-on-line as has been observed for

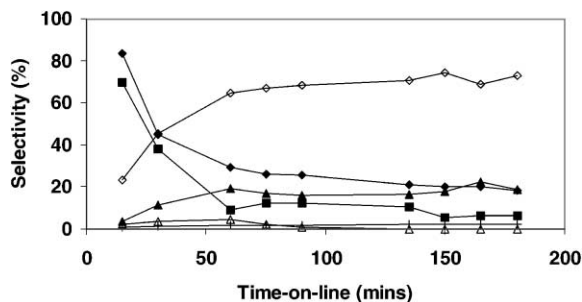


Fig. 1. Conversion of but-2-enal over Co/Al<sub>2</sub>O<sub>3</sub> catalyst at 120 °C. Key: (◆) conversion; product selectivity: (◇) butanal; (■) butanol; (▲) but-2-en-1-ol; (△) 2-ethyl-2-hexanal; (+) propane and butane.

Cu/Al<sub>2</sub>O<sub>3</sub> catalysts in related studies [13–16]. As the catalysts deactivate, the selectivity to butanal and but-2-en-1-ol increases at the expense of the total hydrogenation product butanol and the minor by-product 2-ethyl-2-hexenal, which is formed by dimerisation (Fig. 1). In addition, minor by-products of propane and butane formed by hydrogenation and hydrogenolysis were also observed (1–2% selectivity) and the formation of these products remained unaffected by the deactivation process. The effect of thiophene modification is shown in Fig. 2. The effect is very marked and leads to a distinct loss in conversion, but a steady low conversion of 2–3% is now observed. The hydrogenation products are now exclusively butanal (84%) and but-2-en-1-ol (15%), together with a very low (ca. 1%) selectivity to propane and butane. The effect of thiophene modification of the Co/SiO<sub>2</sub> catalyst is

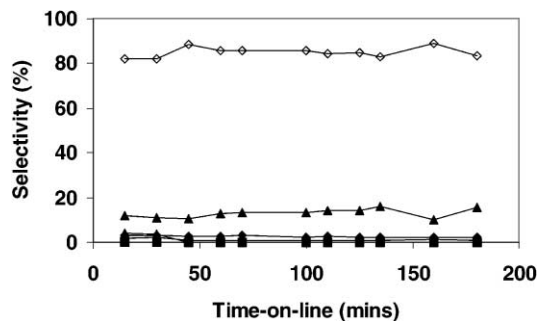


Fig. 2. Conversion of but-2-enal over thiophene-modified Co/Al<sub>2</sub>O<sub>3</sub> catalyst at 120 °C. Key: (◆) conversion; product selectivity: (◇) butanal; (■) butanol; (▲) but-2-en-1-ol; (△) 2-ethyl-2-hexanal; (+) propane and butane.

Table 1  
Effect of thiophene modification on the hydrogenation of but-2-enal over Co/SiO<sub>2</sub> and Co/ZnO catalysts at 120 °C

Time-on-line (min)	Conversion (%)	Product selectivity (%)			
		Butanal	Butanol	But-2-en-1-ol	Others
Co/SiO <sub>2</sub> unmodified					
15	24.0	56.8	17.8	23.5	2.0
30	19.4	57.7	11.6	28.7	2.0
45	17.3	57.5	8.6	31.9	2.0
60	16.9	56.3	10.7	31.0	2.0
120	13.3	55.2	9.6	33.1	2.0
180	10.7	54.2	6.5	37.3	2.0
Co/SiO <sub>2</sub> thiophene-modified					
15	15.2	91.5	2.3	0.0	0.2
30	14.0	99.1	0.9	0.0	0.0
45	13.7	100	0.0	0.0	0.0
60	11.4	100	0.0	0.0	0.0
120	10.3	100	0.0	0.0	0.0
180	8.0	100	0.0	0.0	0.0
Co/ZnO unmodified					
30	14.4	57.7	13.4	27.1	1.8
60	15.6	57.0	14.1	26.9	2.0
120	15.9	55.9	14.5	27.7	1.9
Co/ZnO thiophene-modified					
30	13.8	81.8	1.1	14.6	2.5
60	13.0	77.8	4.7	16.2	1.3
120	15.6	76.5	3.7	16.4	1.4

more marked and now the catalyst exclusively forms butanal with a slight loss in conversion (Table 1). For Co/ZnO, thiophene modification does not significantly affect the conversion but, again, the selectivity to butanal is enhanced. Ni/Al<sub>2</sub>O<sub>3</sub> is more active as a catalyst for but-2-enal hydrogenation, but the major product formed is butanol. Thiophene modification of Ni/Al<sub>2</sub>O<sub>3</sub> resulted in a decrease in conversion and a shift in the product distribution to the almost exclusive formation of butanal (Table 2). In contrast, the modification of Pd/Al<sub>2</sub>O<sub>3</sub> with thiophene did not lead to a loss of conversion but enhanced the formation of butanal at steady state conditions, although, initially the dimerisation product, 2-ethylhexanal, was observed in significant amounts (Table 3).

With unmodified Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub>, butanol is initially a major product but the catalysts deactivate during the timescale of the experiment and butanal is then formed (Table 4). For the Pt/Al<sub>2</sub>O<sub>3</sub>, Ru/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, the effect of thiophene modification is not pronounced in the formation of the

main products, although, the selectivity to butanal is enhanced with some loss in conversion (Table 4). The main effect, particularly marked for Rh/Al<sub>2</sub>O<sub>3</sub>, is the decrease in the products of the dimerisation reactions or the by-products formed by hydrogenation and hydrogenolysis (propane and butane). In general, the decrease in by-product formation is observed for all the catalysts examined and the effects of thiophene modification at steady state conversion are shown in Fig. 3. For comparison, the effect of thiophene modification for a 5 wt.% Cu/Al<sub>2</sub>O<sub>3</sub> is also shown for the same reaction and modification conditions. With the exception of the Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, the main effect of thiophene modification appears to enhance the selectivity for C=C bond hydrogenation to give butanal rather than C=O bond hydrogenation to give but-2-en-1-ol. The effect of the modification with sulphur is, therefore, to enhance the selectivity of the formation of the expected hydrogenation product, although, as this is observed with a loss of conversion, it is apparent that sulphur acts as a poison for these catalysts and the

Table 2

Effect of thiophene modification in the hydrogenation of but-2-enal over Ni/Al<sub>2</sub>O<sub>3</sub> at 120 °C

Time-on-line (min)	Conversion (%)	Product selectivity <sup>a</sup> (%)					
		Butanal	Butanol	But-2-en-1-ol	2E2H	2EH	Others
Unmodified							
15	100	19.5	80.2	0.0	0.0	0.0	0.3
30	100	17.4	82.3	0.0	0.0	0.0	0.3
45	100	16.9	82.8	0.0	0.0	0.0	0.2
60	100	17.1	82.7	0.0	0.0	0.0	0.2
180	100	15.8	83.7	0.0	0.0	0.0	0.3
Thiophene-modified							
15	39.5	89.5	0.3	Trace	4.3	5.5	0.5
30	41.0	88.2	1.0	0.2	9.4	1.1	0.1
45	33.5	95.6	0.8	0.3	2.7	0.3	0.2
60	26.6	99.8	0.0	0.0	0.0	0.0	0.2
180	7.2	100	0.0	0.0	0.0	0.0	0.0

<sup>a</sup> 2E2H: 2-ethyl-2-hexenal, 2EH: 2-ethylhexanal, others: propane and butane.

yield of butanal is lower in the presence of sulphur. For Cu/Al<sub>2</sub>O<sub>3</sub> catalysts, the effect of sulphur modification is to create sulphur promoted Cu<sup>δ+</sup> sites, identified by FTIR spectroscopy, that are both active and selective for C=O bond hydrogenation. A related study using Co/SiO<sub>2</sub> catalysts showed that thiophene modification effectively poisoned all the Co sites present equally [20] and, hence, no selectivity could be expected to be induced for the hydrogenation of C=O

bonds with Co/SiO<sub>2</sub> catalysts, and this is observed. It is apparent that Ni, Pd, Pt, Ru and Rh catalysts behave in a similar manner to Co/SiO<sub>2</sub> and that the electronically promoted M<sup>δ+</sup> sites are not induced on the surface of these crystallites. Hence, it can be concluded that the beneficial effects of sulphur modification of metal catalysts to promote the selective hydrogenation of the C=O bond of α,β-unsaturated aldehydes can be expected to be restricted to supported Cu and Au

Table 3

Effect of thiophene modification on the hydrogenation of but-2-enal over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts at 120 °C

Time-on-line (min)	Product selectivity <sup>a</sup> (%)				
	Butanal	Butanol	But-2-en-1-ol	2EH	Others
Unmodified					
15	47.4	29.2	5.8	16.7	1.0
30	62.1	26.9	2.7	7.2	1.1
45	77.5	17.9	0.7	2.9	0.9
60	85.0	13.6	0.1	0.5	0.8
120	91.5	7.4	0.0	0.2	0.8
180	93.3	5.7	0.0	0.1	0.7
Thiophene-modified					
15	51.3	8.4	0.0	38.8	1.5
30	62.0	3.9	0.0	33.0	1.1
45	99.0	Trace	0.0	Trace	1.0
60	95.9	1.3	0.0	2.1	0.7
120	98.0	0.9	0.0	0.6	0.7
180	98.2	0.8	0.0	0.4	0.6

<sup>a</sup> All at 100% conversion, 2EH: 2-ethylhexanal.

Table 4  
Effect of thiophene modification on the hydrogenation of but-2-enal over Pt, Ru and Rh catalysts

Time-on-line (min)	Conversion (%)	Product selectivity <sup>a</sup> (%)					
		Butanal	Butanol	But-2-en-1-ol	2E2H	2EH	Others
<b>Pt/Al<sub>2</sub>O<sub>3</sub> unmodified</b>							
15	89.7	29.4	57.6	4.1	4.5	0.0	6.4
60	49.9	63.6	23.3	8.4	0.0	0.0	4.7
120	38.0	75.2	9.4	9.7	0.0	0.0	5.7
<b>Pt/Al<sub>2</sub>O<sub>3</sub> thiophene-modified</b>							
15	78.3	26.7	57.5	9.4	2.1	1.9	2.4
60	24.7	80.2	8.0	9.4	0.0	0.0	2.3
120	23.6	81.7	4.4	11.5	0.0	0.0	2.4
<b>Ru/Al<sub>2</sub>O<sub>3</sub> unmodified</b>							
15	10.3	85.6	0.0	8.6	0.0	0.0	5.8
60	10.5	85.1	0.0	9.1	0.0	0.0	5.7
120	7.2	86.3	0.0	6.3	0.0	0.0	7.3
<b>Ru/Al<sub>2</sub>O<sub>3</sub> thiophene-modified</b>							
15	12.2	90.6	0.0	4.2	0.0	0.0	1.8
60	8.8	91.1	0.0	3.5	0.0	0.0	3.4
120	6.4	92.0	0.0	3.8	0.0	0.0	4.2
<b>Rh/Al<sub>2</sub>O<sub>3</sub> unmodified</b>							
15	100	15.2	25.5	25.6	0.2	29.5	3.6
60	100	63.7	12.6	7.3	3.6	10.2	2.6
120	88.9	81.2	9.3	2.6	0.6	4.6	1.6
<b>Rh/Al<sub>2</sub>O<sub>3</sub> thiophene-modified</b>							
15	69.0	82.3	9.2	0.0	1.7	4.7	2.0
60	75.7	91.9	3.9	0.3	0.3	1.3	1.8
120	64.3	95.4	1.5	0.3	0.4	0.2	2.2

<sup>a</sup> 2E2H: 2-ethyl-2-hexanal, 2EH: 2-ethylhexanal, others: propane and butane.

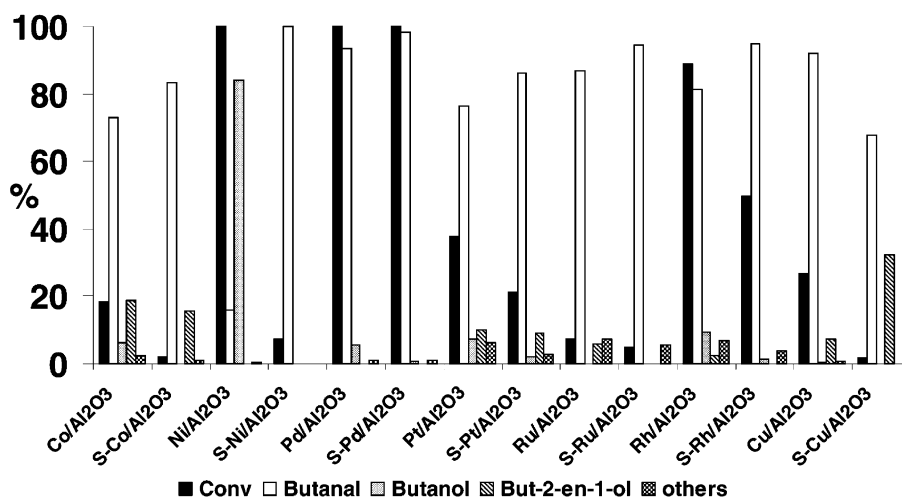


Fig. 3. Comparison of the effect of thiophene-modification on the hydrogenation of but-2-enal at steady state conversion at 180 min time-on-line.

catalysts [3–17] for which sulphur appears to act as an electronic promoter.

### Acknowledgements

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