JOURNAL OF CATALYSIS **148**, 453–463 (1994)

Selectivity Enhancement in the Hydrogenation of α, β-Unsaturated Aldehydes and Ketones Using Thiophene-Modified Catalysts

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Received June 16, 1993; revised February 28, 1994

The hydrogenation of a series of α,β-unsaturated aldehydes and ketones has been studied over 5% Cu/Al_2O_3 and thiophene-modified 5% Cu/Al_2O_3 catalysts. For a series of α,β-unsaturated aldehydes with increasing methyl group substitution of the carbon–carbon double bond, acrolein, crotonaldehyde, 2-methylbut-2-enal, and 3-methylbut-2-enal, in the absence of thiophene modification, the reaction products are found to be mainly the corresponding alcohol, i.e., the product of total hydrogenation, or the aldehyde, i.e., the product of carbon–carbon double bond hydrogenation. Following treatment with thiophene (1 μl/0.1 g 5% Cu/Al_2O_3), a significant enhancement in the rate of unsaturated alcohol formation is observed, which is particularly pronounced for acrolein and crotonaldehyde. Evidence is provided to demonstrate that the effect is caused by an enhancement in the rate of unsaturated alcohol formation and not by a decrease in the rate of hydrogenation of this species. Similar experiments with α,β-unsaturated ketones do not give the same enhancement in the synthesis of the unsaturated alcohol. The catalytic observations are combined with the results of FTIR spectroscopic characterisation of thiophene-treated and untreated Cu/Al_2O_3 using carbon monoxide as a probe molecule. The origin of the enhancement in selectivity is discussed in terms of geometric and electronic effects. © 1994 Academic Press, Inc.

INTRODUCTION

The use of heterogeneous catalysts in the production of fine chemicals has been an important topic for many years. In particular, control of product selectivity in oxidation and reduction reactions is considered to be extremely important. An example of such selectivity control is the selective hydrogenation of α,β-unsaturated aldehyde to the corresponding unsaturated alcohol. This reaction requires the selective hydrogenation of the carbonyl group in preference to the hydrogenation of the carbon–carbon double bond. A number of studies have addressed this challenging task (1–6). Previous studies have utilised supported metal catalysts in which the support is considered to play an important role in controlling the catalyst morphology. In addition the use of mixed metal catalysts and alkali-promoted catalysts has also been studied. For example, it has been shown that the carbonyl group in crotonaldehyde can be preferentially hydrogenated to form crotyl alcohol by $Ni–Cu/Al_2O_3$ (1), Pt/TiO_2 (2), $Pt–Fe/SiO_2$ (3), and Cu/Cr_2O_3 (4). Recently, it has been shown that the addition of potassium to Ru/SiO_2 or Ru/Zeolite-Y resulted in a marked change in product selectivity for the hydrogenation of 3-methylbut-2-enal (5). In this case, the potassium was considered to enhance reactant adsorption and subsequent polarization of the carbonyl group.

Most recently Marinelli *et al.* (6) have studied the influence of alloying, sulphur poisoning and transition metal additives on the hydrogenation of acrolein over Pt catalysts. They found that alloying and notably catalyst poisoning did not induce significant selectivity enhancement for allyl alcohol synthesis, but they did observe some enhancement when oxides of Ge, Ga, and Sn were added. We have adopted a different approach to inducing selectivity enhancement in the hydrogenation of α,β-unsaturated compounds, namely, the partial poisoning of a supported copper catalyst using sulphur compounds. Copper catalysts are known to be active for a number of hydrogenation reactions (7) and are also known to be extremely sensitive to the presence of very low levels of sulphur poisons (7). To date, there have been no detailed reports concerning the effect of partially poisoning a catalyst as a means of improving selectivity in the hydrogenation of α,β-unsaturated compounds. Although variations in product selectivity induced by catalyst poisoning have been widely studied (8), most reported work has concerned alkene hydrogenation and the effect of sulphur on the activity and selectivity for alkane hydrogenation (9).

0021-9517/94 $6.00

We have found, in contrast to Marinelli *et al.* (6), that partial sulphur poisoning of a hydrogenation catalyst can induce marked selectivity changes (10). In this paper, we describe in detail the studies carried out on thiophene modification of a 5% Cu/Al_2O_3 catalyst for the hydrogenation of a range of α,β-unsaturated aldehydes and ketones.

EXPERIMENTAL

The catalyst, 5% Cu/Al_2O_3, was prepared according to the following procedure. γ-Alumina (Condea SCF, Puralox ScFa-140) was added to an aqueous solution of copper(II) nitrate (Aldrich, 99.999%) so as to yield 5 wt% Cu metal. The slurry was stirred at 80°C and allowed to evaporate to give a thick paste, which was then dried (100°C, 16 h) and calcined (450°C, 16 h).

For the infrared study, a self-supporting disc was formed by pressing 0.1 g of the catalyst precursor between two 25-mm-diameter polished steel dies at ca. 2 MPa. The catalyst disc was mounted in a glass IR cell which allowed measurement of the IR spectra while being heated. This cell was linked to a vacuum line capable of achieving pressures of <ca. 10^{-3} Pa. Infrared spectra were recorded using a Perkin–Elmer model 1720X FTIR spectrometer, coupled to a Perkin–Elmer series 7700 computer. The disc was calcined in a flow of air (100 cm^3 min^{-1}) at 310°C for 16 h. The sample was then reduced at 210°C in a flow of hydrogen (BOC, 99.995%, 100 ml min^{-1}), which had previously passed through a deoxo unit (Anco Gas Engineering Ltd.) and a molecular sieve to remove oxygen and water impurities. After reduction, the sample was evacuated at 210°C for 1 h prior to cooling to ambient temperature.

For catalytic study the catalyst (0.1 g) was introduced to the reactor tube (10 mm i.d.) and held in place by a quartz frit. The sample was then reduced *in situ* in hydrogen (3.6 l h^{-1}) at 210°C for 16 h. These reduction conditions were selected on the basis of previous studies (10). Following reduction, the temperature was adjusted to the required temperature for catalytic reaction. α,β-unsaturated compounds, e.g., crotonaldehyde, were introduced into the reactor system via a calibrated syringe pump and vaporised in the preheated reactor inlet zone. Hydrogen was utilised as both reactant and carrier gas and an H_2 : crotonaldehyde ratio of 14 : 1 was used in all experiments. Modified catalysts were prepared by injection of thiophene or thiophene/pentane solution (0.1–1 μl) directly on to the reduced catalyst in the hydrogen carrier flow. Products were analysed using on-line gas chromatography using thermal conductivity and flame photometric detectors. Satisfactory mass balances were obtained and the experimental errors associated with the conversion and selectivity data reported in this paper are $\leq \pm 1\%$.

RESULTS

Hydrogenation of Crontonaldehyde

The effect of reaction temperature on the hydrogenation of crotonaldehyde over 5% Cu/Al_2O_3 in the presence and absence of thiophene is shown in Table 1. For this hydrogenation reaction, there are three possible reaction products, crotyl alcohol, butanal, and 1-butanol. In the absence of thiophene, crotonaldehyde conversion increases rapidly from 60 to 150°C and the selectivity to 1-butanol also increases in a similar manner. In general at low conversion the main product is butanal and crotyl alcohol is only observed in minor amounts (<10%). Hence, 5% Cu/Al_2O_3 preferentially hydrogenates the carbon-carbon double bond rather than the carbonyl group. Treatment of the catalyst with thiophene (1 μl/0.1 g Cu/Al_2O_3 and 2 μl/0.1 g Cu/Al_2O_3) significantly changes the catalytic performance of the hydrogenation of crotonaldehyde both with respect to product selectivity and yield. In particular, the conversion is markedly decreased in the presence of thiophene as is expected from the known poisoning effect of sulphur compounds on copper catalysts for a number of reactions (7, 8). However, sufficient catalyst activity is retained and it is apparent that the selectivity to both 1-butanol and butanal is decreased and the selectivity to crotyl alcohol is enhanced so that it becomes the dominant product. Comparison of results at similar conversions and constant temperature for untreated and thiophene modified catalysts (Fig. 1) indicates that the enhancement in crotyl alcohol selectivity is not related to the decreased conversion. In addition, comparison of data at the same reaction condition (temperature, WHSV, and time-on-line) indicates that the yield of crotyl alcohol is increased on the addition of thiophene, indicating an increase in the rate of production of this product even though the overall conversion is decreased.

The effect of time-on-line is shown in Table 1 and also in Fig. 2. Deactivation of the catalyst with and without

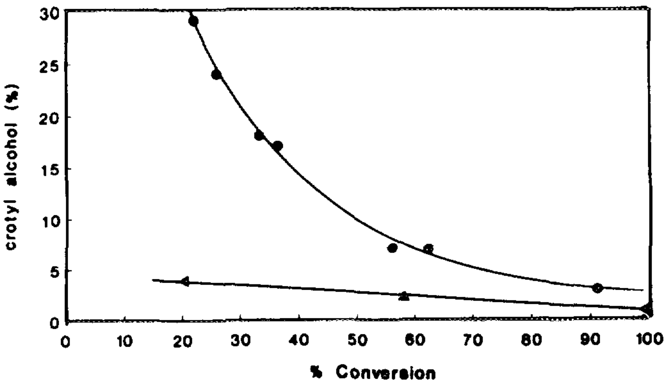

FIG. 1. Crotyl alcohol selectivity versus conversion of crotonaldehyde at constant temperature of 150°C for (●) thiophene-treated and (▲) untreated Cu/Al_2O_3 catalyst.

TABLE 1

Effect of Thiophene Addition on the Hydrogenation of Crotonaldehyde over Cu/Al_2O_3 Catalysts[a]

		Thiophene/µl														
		0					1					2				
			Product selectivity (%)					Product selectivity (%)					Product selectivity (%)			
T (°C)	Time-on-line (min)	Conv. (%)	Crotyl alcohol	Butanal	Butanol	Others[b]	Conv. (%)	Crotyl alcohol	Butanal	Butanol	Others[b]	Conv. (%)	Crotyl alcohol	Butanal	Butanol	Others[b]
60	15						3.5	44	25	32	—					
	30						2.1	52	28	20	—					
	60						1.0	40	31	—	29					
	120						0.9	22	30	—	49					
	180						0.4	36	64	—	—					
80	15	8.0	10	59	27	5	3.1	64	25	—	11	9.5	40	15	27	18
	30	5.9	10	77	6	8	1.7	43	41	—	16	4.8	58	20	16	6
	60	4.5	—	89	—	11	1.5	29	35	—	35	3.9	50	21	5	24
	120	4.9	11	75	—	14	1.2	36	34	—	29	2.7	41	26	—	33
	180	3.9	—	88	—	12	—	—	—	—	—	2.6	37	25	—	38
100	15	15.7	7	83	7	3	6.6	33	35	24	8	10.5	53	17	14	16
	30	14.1	13	83	—	4	3.9	39	46	—	15	5.5	53	28	—	19
	60	15.8	9	87	—	4	3.7	38	42	—	20	4.2	56	23	—	21
	120	14.1	8	88	—	4	2.8	27	45	—	28	—	—	—	—	—
	180	15.5	12	86	—	3	2.3	28	43	—	29	5.0	42	35	—	23
120	15	54.0	3	69	18	10	13.3	32	52	8	9	10.7	36	43	10	11
	30	49.1	5	83	11	1	10.0	32	58	—	10	8.4	38	48	5	9
	60	44.6	6	84	6	4	7.6	33	57	—	10	6.2	35	55	—	10
	120	41.3	9	85	4	1	7.5	31	57	—	12	5.6	32	56	—	12
	180	39.1	10	86	3	1	7.0	28	58	—	14	5.0	33	54	—	13
150	15	100	1	0.3	95	3.7	54.8	15	65	19	1	26.5	22	59	8	11
	30	100	1	1	98	—	26.1	29	59	4	8	25.7	24	62	6	8
	60	100	0.6	22	77		27.4	25	67	4	4	21.7	30	62	—	8
	120	100	1	49	50	—	24.7	23	66	3	8	20.4	28	63	2	7
	180	100	1.6	55	43		25.4	27	64	1	8	19.9	28	62	2	8

[a] WHSV = $1.2\ h^{-1}$; crotonaldehyde : H_2 = 1 : 14.

[b] Aldol condensation products.

thiophene treatment is rapid during the initial stage of the reaction (5–30 min), but is relatively stable following this initial period. Selectivity changes during the initial reaction period are marked, since at 80°C in the absence of thiophene (Fig. 2) the initial product is mainly 1-butanol, but as the catalyst ages the major product becomes butanal. In the presence of thiophene (Fig. 2) the initial high selectivity to 1-butanol is also observed, but on ageing the major product is now crotyl alcohol. It is clear that significant selectivity variations are observed during this

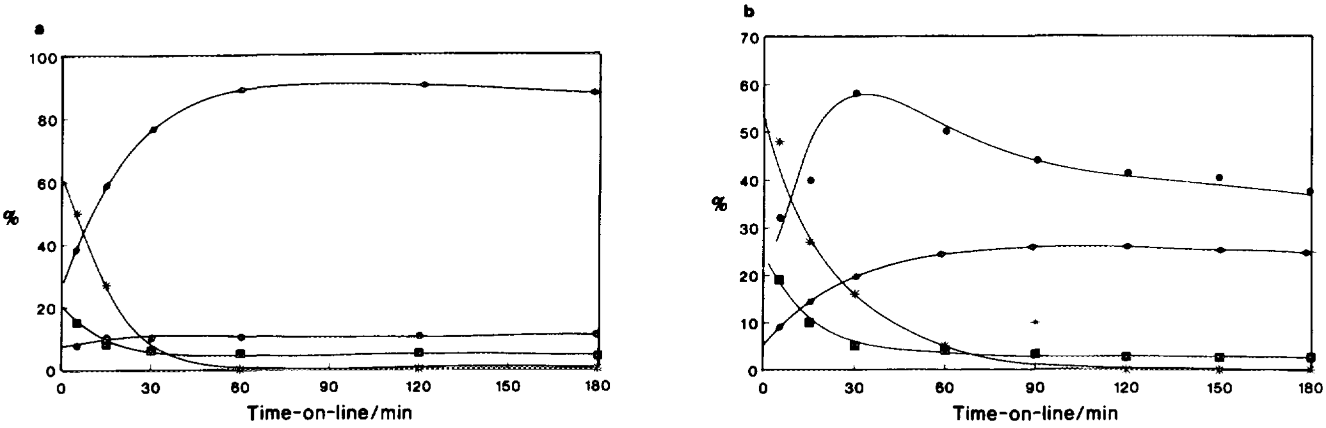

FIG. 2. (a) Effect of time-on-line on the activity and selectivity of Cu/Al_2O_3 catalyst reduced at 210°C, reaction temperature = 80°C; H_2 : crotonaldehyde = 14 : 1; WHSV = $1.26\ h^{-1}$. Key: (●) crotyl alcohol, (◆) butanal, (*) butanol, and (■) conversion. (b) Effect of time-on-line on the activity and selectivity of Cu/Al_2O_3 catalyst treated with 2 µl thiophene at 210°C; reaction temperature = 80°C; H_2 : crotonaldehyde = 14 : 1; WHSV = $1.26\ h^{-1}$. Key as (a).

initial period of reaction time. In part, these are due to coke formation on the catalyst surface resulting from aldol condensation reactions of the reactants and intermediates. Treatment of the catalyst with thiophene leads to only a slight enhancement in coke formation and hence the effect of coke deposition can be considered to be similar for both thiophene-treated and untreated catalysts. For the untreated catalyst the rate of coke deposition is 2.5×10^{-2} mg C/100 mg/min for reaction of crotonaldehyde at WHSV = 1.2 h^{-1} and 150°C. Under comparable conditions, the catalyst modified with 1 μl thiophene gives a rate of coke formation of 2.8×10^{-2} mg C/100 mg/min.

The effect of the temperature of treatment with thiophene is shown in Fig. 3. In general crotonaldehyde conversion decreases with increasing treatment temperature for the same amount of added thiophene. In addition, selectivity changes are also induced on increased temperature of thiophene treatment, and in general the selectivity to crotyl alcohol is enhanced mainly at the expense of butanal.

The effect of the level of thiophene is shown in Fig. 4 for reaction at 150°C. In these experiments the thiophene was added in a single aliquot to the catalyst at 210°C following catalyst reduction at 210°C. This temperature was selected for study since the unmodified 5% Cu/Al_2O_3 catalyst was found to demonstrate low selectivity for crotyl alcohol. Increasing the amount of thiophene leads to an increase in crotyl alcohol selectivity and the conversion of crotonaldehyde decreases. A further set of experiments was conducted (Fig. 5) in which higher concentrations of thiophene were added using multiple injection of 1 μl thiophene. Increasing the amount of thiophene further enhances crotyl alcohol selectivity at the expense of butanal.

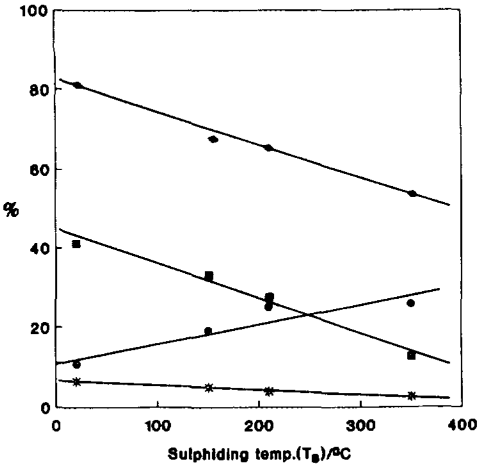

FIG. 3. Effect of treatment temperature on the activity and selectivity of Cu/Al_2O_3 catalyst; results obtained at reaction temperature of 150°C and 60 min time-on-line; H_2 : crotonaldehyde = 14 : 1. Key as in Fig. 2a.

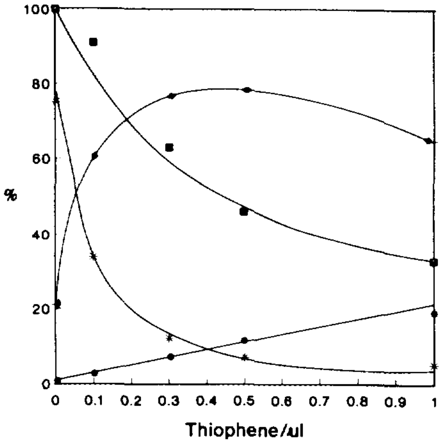

FIG. 4. Effect of single pulses of thiophene on crotonaldehyde hydrogenation over Cu/Al_2O_3 catalyst treated at 210°C; reaction temperature = 150°C; H_2 : crotonaldehyde = 14 : 1; WHSV = 1.2 h^{-1}. Key: (●) crotyl alcohol, (◆) butanal, (*) butanol, and (■) conversion.

A sulphur-sensitive flame photometric detector was utilised to determine the amount of thiophene adsorbed by the catalyst (Fig. 6). At low thiophene levels, up to 1 μl, >90% of the thiophene is adsorbed on the catalyst, whereas additional injection of 1 μl of thiophene results in only a small amount of additional thiophene adsorption. During the subsequent hydrogenation reaction, sulphur could not be detected in the reaction products (level of detection 1 ppm) and consequently it is concluded that the sulphur is retained on the catalyst under reaction conditions.

Hydrogenation of Butanal and Crotyl Alcohol

The hydrogenations of butanal and crotyl alcohol were investigated at 80 and 150°C and the results are shown in Table 2. Butanal hydrogenation in the absence of thio-

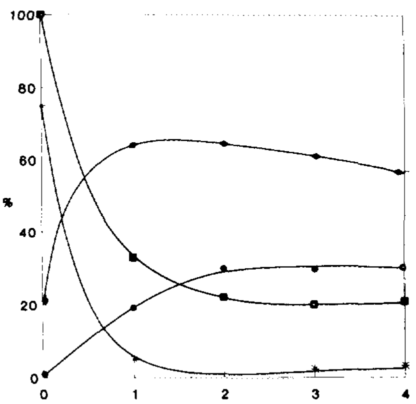

FIG. 5. As for Fig. 4 but with multiple pulses of thiophene at 1 μl per pulse.

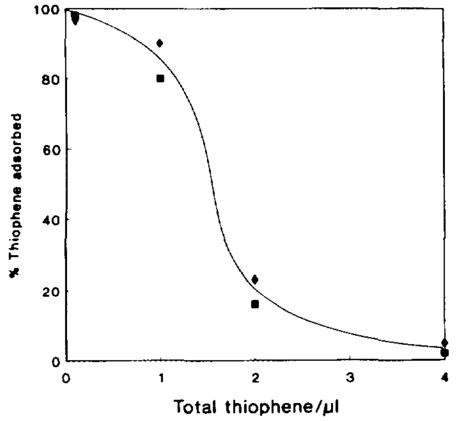

FIG. 6. Effect of temperature on thiophene adsorption over reduced Cu/Al_2O_3 determined by FPD: (■) 150°C and (◆) 210°C.

phene gives mainly 1-butanol, but some additional products were also formed mainly due to aldol condensation reactions. On addition of thiophene (1 µl/0.1 g Cu/Al_2O_3) the conversion is decreased and in addition the selectivity to 1-butanol decreases and additional products are formed. An experiment in the absence of hydrogen but using helium demonstrated that the formation of the butyl butanoate and the additional condensation products was catalysed by the Cu/Al_2O_3 catalyst and that this competitive reaction was not particularly affected by the addition of thiophene. The conversion of butanal to crotonaldehyde or crotyl alcohol was not observed with the experimental conditions examined. The effect of time-on-line on the hydrogenation of butanol at 120°C is shown in Fig. 7. In the absence and presence of sulphur, catalyst deactivation is observed during the initial 60-min operation, and following that time the catalytic performance was observed to be fairly stable. Crotyl alcohol hydrogenation in the absence of thiophene is observed to give 1-butanol, butanal and crotonaldehyde as products; in addition, as for butanal, a range of other products is also observed. Addition of thiophene does not significantly affect the steady state conversion (Fig. 8) but does in-

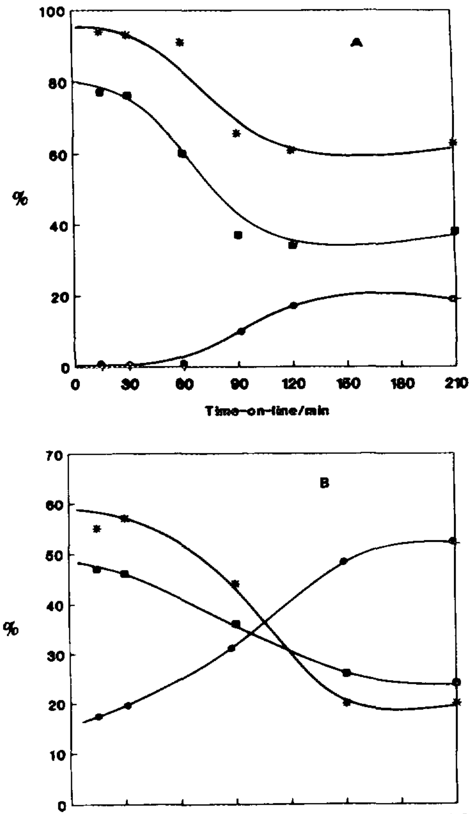

FIG. 7. Effect of time-on-line on butanal hydrogenation over Cu/Al_2O_3 catalyst; (A) untreated and (B) treated with 1 µl thiophene at 210°C; reaction temp. = 120°C, H_2 : butanal 14 : 1; WHSV = 1.3 h^{-1}. Key: (*) butanol, (●) butyl butanoate, and (■) conversion.

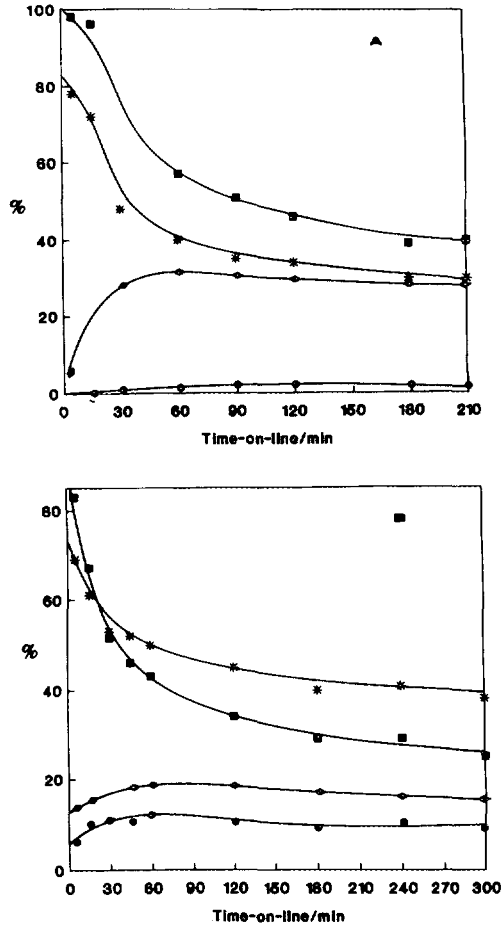

FIG. 8. Effect of time-on-line on crotyl alcohol hydrogenation over Cu/Al_2O_3 catalyst (A) untreated and (B) treated with 1 µl thiophene at 210°C; reaction temp. = 120°C; H_2 : crotyl alcohol = 14 : 1. Key: (●) crotonaldehyde, (◆) butanal, (*) butanol, and (■) conversion.

TABLE 2

Conversion of Butanal and Crotyl Alcohol over Unsulphided and Sulphided Cu/Al_2O_3 Catalyst[a]

Catalyst	Reactant	T (°C)	Conv. (%)	Product selectivity (%)					
				Crotonaldehyde	Crotyl alcohol	Butanal	Butanol	Butyl butanoate	Condensation by-products
Cu/Al_2O_3	Butanal + H_2	80	28	—	—	—	83	—	17
		100	34	—	—	—	84	—	16
		120	60	—	—	—	92	—	8
		150	100	—	—	—	96	—	4
S–Cu/Al_2O_3	Butanal + H_2	80	25	—	—	—	24	51	25
		100	35	—	—	—	19	53	28
		120	39	—	—	—	68	13	19
		150	44	—	—	—	82	5	13
Cu/Al_2O_3	Crotyl alcohol + H_2	80	34	3	—	28	23	—	45
		100	42	1	—	30	37	—	32
		120	57	1	—	31	41	—	27
		150	93	—	—	16	62	—	22
Cu/Al_2O_3	Crotyl alcohol + He	150	62	10	—	21	9	—	22
		120	27	1	—	—	—	—	26
S–Cu/Al_2O_3	Crotyl alcohol + H_2	80	28	14	—	17	31	—	38
		100	36	10	—	9	56	—	25
		120	43	10	—	19	50	—	21
		150	72	22	—	8	51	—	20

[a] S is 1 μl thiophene adsorbed at 210°C; T is hydrogenation temperature; H_2 : reactant = 14 : 1; WHSV = 2.5 h^{-1}; data obtained at 60 min time-on-line.

crease the selectivity to crotonaldehyde. An experiment in the absence of hydrogen (Table 2) showed that the formation of crotonaldehyde was catalysed by the 5% Cu/Al_2O_3 catalyst. At first sight, it might appear that dehydrogenation of crotyl alcohol was occurring. However, it is more likely that a bimolecular disproportionation may occur to produce crotonaldehyde and butanol:

$$2 \text{ crotyl alcohol} \rightleftharpoons \text{crotonaldehyde} + \text{butanol}.$$

Significantly, the formation of 1-butanol from crotyl alcohol does not appear to be significantly influenced by the addition of thiophene.

Kinetic Scheme for the Hydrogenation of Crotonaldehyde

It is possible to construct a reaction scheme for the hydrogenation of crotonaldehyde based on the results obtained in this study for the hydrogenation of crotonaldehyde, butanal and crotyl alcohol. The scheme (Fig. 9) represents two series of consecutive reactions since butanol can be formed from the hydrogenation of crotyl alcohol via either crotyl alcohol or butanal as intermediates. In addition, our studies have shown that over Cu/Al_2O_3 and Cu/Al_2O_3 modified with thiophene, butanal can be formed from either crotonaldehyde or crotyl alcohol. Also our studies have shown that there is a route from crotyl alcohol to crotonaldehyde. Hence, the overall scheme consists of six reactions which can be represented by six rate constants: k_1, k_2, k_{-2}, k_3, k_4, and k_5. In this simple representation of the reaction scheme, the formation of by-products via condensation reactions has been excluded. Since hydrogen is present in excess, it is possible to consider the scheme (Fig. 9) as a series of consecutive and competing pseudo-first-order reactions. In addition the energy of activation for the hydrogenation of crotonaldehyde was 50 kJ mol^{-1} for unmodified 5% Cu/Al_2O_3, 60 kJ mol^{-1} for 5% Cu/Al_2O_3 modified with 0.5 μl thiophene/0.1 g catalyst, and 63 kJ mol^{-1} for 5% Cu/Al_2O_3 modified with 1.0 μl thiophene/0.1 g catalyst. Hence, it is consid-

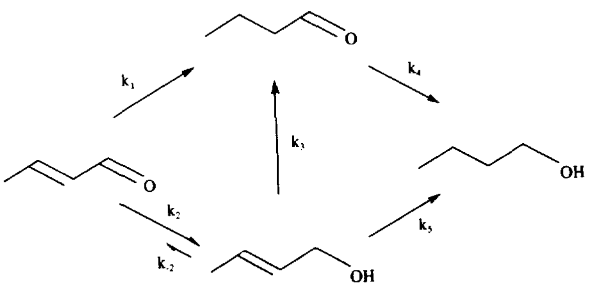

FIG. 9. Reaction scheme for the hydrogenation of crotonaldehyde (formation of by-products, e.g., butyl butanoate, is not included).

ered that diffusion limitations are not present for the reaction conditions selected in this study. The pseudo-first-order rate constants are obtained in the following manner. Initially, k_{-2}, k_3, k_4, and k_5 are determined from experiments using butanal and crotyl alcohol as separate reactants. From the data for crotonaldehyde hydrogenation, an overall value of $k_1 + k_2$ is obtained. The ratio of k_1/k_2 is then obtained from a knowledge of the kinetic equations for the rate of product formation using an iterative process to obtain a best fit value. Values for the rate constants are shown in Table 3.

It is apparent that on modification of Cu/Al_2O_3 with thiophene the rate of butanal hydrogenation to 1-butanol is significantly decreased, whereas the rate of crotyl alcohol hydrogenation to 1-butanol is largely unaffected. In addition, it is observed that the rate of crotyl alcohol formation is significantly enhanced, and it can be concluded that the increase in crotyl alcohol is therefore due to a promotion in the rate of formation rather than a poisoning of the hydrogenation reaction leading to the conversion of crotyl alcohol to 1-butanol.

Hydrogenation of α,β-Unsaturated Aldehydes and Ketones

The reactions of a range of α,β-unsaturated aldehydes and ketones with hydrogen were investigated to study the effect of substitution of the carbon–carbon double bond and carbonyl group on the reactivity to hydrogenation (Table 4). All these reactants gave similar effects with time-on-line as previously observed for crotonaldehyde. For acrolein, which represents the molecule with the least degree of substitution, in the absence of thiophene addition the major product is propanal. Propanal is the exclusive product at 80°C. On modification with thiophene (1 μl/0.1 g Cu/Al_2O_3), the conversion of acrolein is significantly decreased, the effect being more pronounced than observed with crotonaldehyde under identical conditions (Table 4). However, there is now an increase in the selectivity to allyl alcohol, and at the lower reaction temperature of 80°C there is a significant increase in the yield of allyl alcohol for the modified catalyst when compared to the unmodified catalyst. These results indicate that the results obtained for crotonaldehyde are not specifically caused by the substitution of the carbon–carbon double bond by a methyl group; i.e., the promotion in the yield of unsaturated alcohol is not solely related to a steric effect. Further substitution of the carbon–carbon double bond was investigated by hydrogenation of 2-methylbut-2-enal and 3-methylbut-2-enal. For 2-methylbut-2-enal, a significant increase in the selectivity to the corresponding unsaturated alcohol was observed for the catalyst treated with thiophene, but the decrease in conversion observed was less pronounced than for crotonaldehyde.

Effect of Catalyst Support

To investigate the effect of the chemical nature of the support used for the copper catalyst a range of supported copper catalysts were prepared using MgO and SiO_2 as supports. The results for the hydrogenation of crotonaldehyde in the presence and absence of thiophene are shown in Table 5; 12% Cu/MgO and 12% Cu/SiO_2 in the absence of thiophene were active hydrogenation catalysts giving high selectivity to butanal, and only very low selectivity to crotyl alcohol was observed. However, on treatment with thiophene the conversion of crotonaldehyde was decreased and the selectivity to crotyl alcohol was significantly enhanced. It is therefore clear that similar effects are observed for thiophene treatment of Cu supported on Al_2O_3, SiO_2 and MgO, indicating that the effect is primarily due to an interaction between copper and sulphur, and any interaction with the support is of secondary importance. Furthermore, similar effects are observed for a standard $Cu\text{-}ZnO/Al_2O_3$ methanol synthesis catalyst which had been exposed to thiophene (Table 5).

IR Characterisation of the Interaction of Thiophene with 5% Cu/Al_2O_3

The effect of thiophene adsorption in the presence of hydrogen was investigated using a reduced sample of 5% Cu/Al_2O_3 in the form of a self-supporting disc. The cata-

TABLE 3

Psuedo-first-Order Rate Constants

Temperature (°C)	Rate constants[a] $k \times 10^{-6}$ (mol g^{-1} atm^{-1} s^{-1})											
	k_1	k_2	k_{-2}	k_3	k_4	k_5	k_1^S	k_2^S	k_{-2}^S	k_3^S	k_4^S	k_5^S
80	0.30	0.095	0.026	1.1	2.6	0.92	0.022	0.13	0.095	0.54	0.66	0.98
100	0.61	0.10	0.011	1.6	3.4	1.9	0.035	0.15	0.093	0.39	0.79	2.4

[a] Calculated on the basis of the series/consecutive reaction scheme in Fig. 9 using suitable approximations and $k = (F/mP) \ln [1/(1 - x_a))$, where F is molar flow rate of reactant, P is pressure (1 atm = 101.325 kPa), m is mass of catalyst and x_a is fractional conversion. ^{S} is sulphided catalyst, 1 μl thiophene adsorbed at 210°C.

TABLE 4

Hydrogenation of α,β-Unsaturated Aldehydes and Ketones over Unsulphided and Sulphided Cu/Al_2O_3 Catalyst[a]

Catalyst	Reactant	T (°C)	Conv. (%)	Product selectivity (%) Saturated aldehyde	Unsaturated alcohol	Saturated alcohol	Condensation by-products
Cu/Al_2O_3	acrolein	150	67	75	7	4	15
		80	9.6	100	—	—	—
S-Cu/Al_2O_3		150	16.6	68	29	—	3
		80	1.1	54	46	—	—
Cu/Al_2O_3	crotonaldehyde	150	100	1	1	98	—
		80	5.9	77	10	6	7
S-Cu/Al_2O_3		150	26	59	29	3	9
		80	1.7	41	43	—	16
Cu/Al_2O_3	2 methyl but-2-enal	150	100	0.4	—	96	3
		80	20	35	31	32	2
S-Cu/Al_2O_3		150	45	43	15	38	4
		80	6	9	41	34	16
Cu/Al_2O_3	3 methyl but-2-enal	150	100	—	—	99	1
		80	17	11	72	7	10
S-Cu/Al_2O_3		150	26	13	49	12	26
		80	19	2	79	—	19
Cu/Al_2O_3	cyclohex-2-enone	150	100	—	—	100	—
		80	100	0.3	0.5	99	—
S-Cu/Al_2O_3		150	44	76	2	12	10
		80	13	44	17	20	19
Cu/Al_2O_3	4 methylpent-3-en-2-one	80	100	8	—	88	4
S-Cu/Al_2O_3		80	48	36	3	12	10
Cu/Al_2O_3	pent-3-en-2-one	80	100	—	—	100	4
$S/Cu/Al_2O_3$		80	13	36	—	13	51

[a] S is 1 μl thiophene adsorbed at 210°C; T is hydrogenation temperature; H_2 : reactant = 14 : 1; results obtained at 30 min time-on-line.

lyst was initially exposed to thiophene (1.33 Pa) at ambient temperature for 5 min followed by flowing hydrogen (100 ml min^{-1}) at the same temperature, and the results are shown in Fig. 10. Bands were observed at 1865(sh), 1650, 1588, 1435, 1406, 1362(sh), 1320, 1253, 1230, and 1082 cm^{-1}. In a separate experiment (11), these bands were also observed under identical conditions for thiophene adsorption on the alumina alone in the absence of Cu.

TABLE 5

Conversion of Crotonaldehyde Over Unsulphided and Sulphided Supported Copper Catalyst[a]

Catalyst	Thiophene presulphiding[b] (μl)	Temperature (°C)	Conv. %	Product selectivity Crotyl alcohol	Butanal	Butanol	Other[c]
12% Cu/MgO	0	150	80	4.0	38.0	52.5	5.5
	1	150	10	38.6	45.5	3.9	12.1
	2	150	5.4	39.7	49.2	0	11.1
12% Cu/SiO_2	0	150	96.5	2.5	59.4	36.9	1.4
	1	150	30.5	15.0	81.1	2.1	1.7
Cu–ZnO/Al_2O_3	0	100	93	4.8	23.5	69.1	2.6
60 : 30 : 10	2	100	8	35.2	41.0	14.2	9.6

[a] WHSV = 1.2 h^{-1}; crotonaldehyde : H_2 = 1 : 14.

[b] Thiophene added after reduction, μl/0.1 g catalyst, 210°C.

[c] Condensation products.

These bands are therefore assigned to interaction of thiophene with the support. Additional bands were observed in the presence of reduced Cu at 1372(sh) and 1191 cm^{-1}. Sexton (12) has observed similar bands for adsorption of thiophene on Cu(100) and these have been assigned to in-plane vibrations of the thiophene ring adsorbed on the copper surface. This indicates that at ambient temperature molecular thiophene is adsorbed on the copper surface.

The temperature was then increased in 25°C increments to 200°C (Fig. 10) and the intensities of the bands assigned to thiophene interacting with the alumina surface decreased. Identical behaviour was noted in the absence of reduced copper. In addition, the intensity of the band at 1191 cm^{-1} decreased to zero at 100°C, indicating the decomposition of the copper-thiophene surface species. On cooling to ambient temperature (Fig. 10), only extremely weak bands were observed in the 1630–1460 cm^{-1} spectral region, which were due to residual adsorption of thiophene on the alumina support. Subsequent adsorption of CO at ambient temperature resulted in a band envelope at 2116, 2124(sh) and 2104 cm^{-1} (Fig. 11). The intensity of this band envelope was more than an order of magnitude less than that observed for a similar experiment in the absence of thiophene (Fig. 12). Bands at 2116 cm^{-1} and 2124(sh) cm^{-1} are indicative of CO bound to copper(I) sites (13–15). This suggests that adsorption of sulphur on to the copper surface involves e^- transfer from the copper surface to the adsorbed sulphur species which is in agreement with work function measurements (16). Such electronic effects are generally considered to be short range (17, 18) and hence these Cu^+ sites must be located close to the adsorbed sulphur atoms. The band at 2104 cm^{-1} is characteristic of a CO–Cu^0 species (19). Hence, the IR experiments indicate that there are a number of surface sites present on the sulphided Cu/Al_2O_3 catalyst in which Cu^0 and Cu^+ are located in close proximity to adsorbed sulphur.

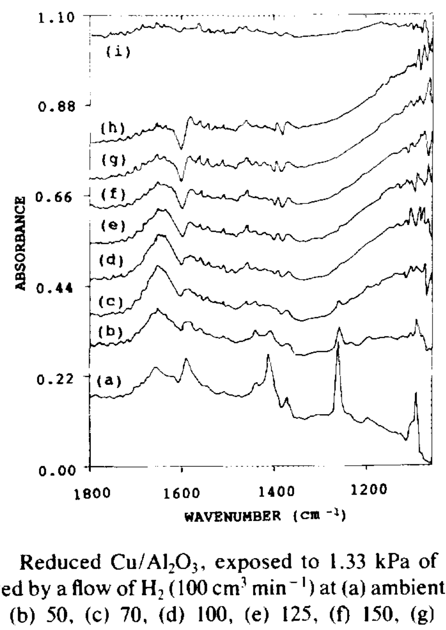

FIG. 10. Reduced Cu/Al_2O_3, exposed to 1.33 kPa of thiophene (5 min) followed by a flow of H_2 (100 cm^3 min^{-1}) at (a) ambient temperature (ca. 22°C), (b) 50, (c) 70, (d) 100, (e) 125, (f) 150, (g) 175, and (h) 200 °C with each sample equilibrated for 10 min; (i) ambient temperature.

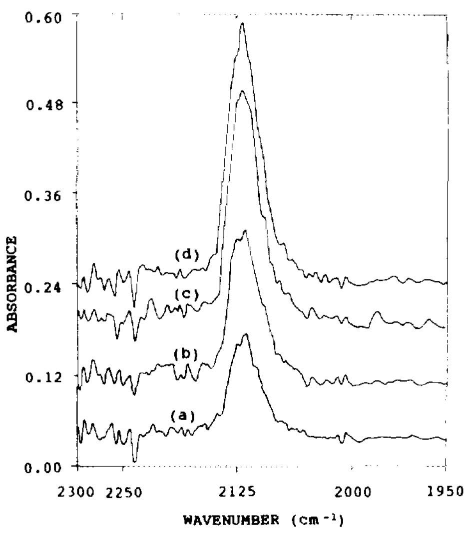

FIG. 11. Reduced Cu/Al_2O_3 exposed to 1.33 kPa of thiophene and a H_2 flow at 200°C, before evacuation and cooling. Exposed to (a) 0.27, (b) 0.53, (c) 1.06, and (d) 1.33 kPa of CO at ambient temperature.

DISCUSSION

The results of this study indicate that modification of Cu/Al_2O_3 catalyst by thiophene can give marked and sustained activity and selectivity effects in the hydrogenation of α,β-unsaturated aldehydes and ketones. For the simplest α,β-unsaturated carbonyl compound studied, i.e., acrolein, the effects are particularly marked. For example, in the absence of thiophene modification, acro-

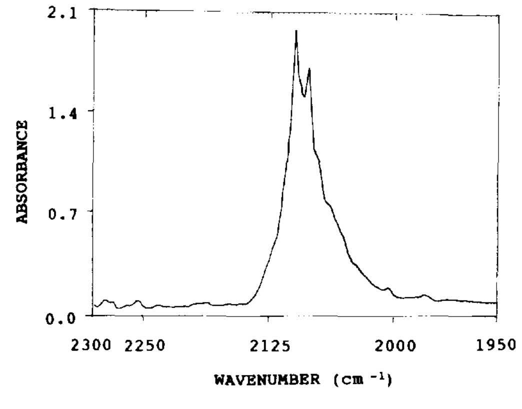

FIG. 12. Reduced Cu/Al_2O_3 in contact with 270 Pa CO at ambient temperature.

lein is exclusively hydrogenated to 1-propanol at 80°C, whereas after treatment with thiophene allyl alcohol is observed as a significant product. It is therefore apparent that modification of the copper catalyst with thiophene has two pronounced effects. First the overall hydrogenation activity is decreased. In the case of acrolein hydrogenation at 80°C, the effect of thiophene treatment is to decrease the catalyst activity by an order of magnitude. Second, modification by thiophene leads to a catalyst that preferentially hydrogenates the carbonyl double bond rather than the carbon–carbon double bond, which is more readily hydrogenated in the absence of sulphur. The effect of thiophene modification becomes less pronounced with methyl group substitution of the carbon–carbon double bond of the α,β-unsaturated aldehyde, as has been previously noted by Marinelli *et al.* (6), although the hydrogenation activity of the catalyst is decreased by thiophene treatment. Methyl group substitution of the carbonyl group, i.e., changing from an aldehyde to a ketone, leads to a system for which the unsaturated alcohol is only a very minor product in comparison to the saturated ketone and alcohol. These changes in selectivity resulting from changes in the stereochemistry of the reactant molecule indicate that steric factors are important in the hydrogenation of α,β-unsaturated compounds on the Cu/Al_2O_3 catalyst.

Use of CO as a probe molecule following exposure of catalyst to thiophene is instructive since the marked decrease observed in the intensity of the CO stretching band envelope between 2200 and 2100 cm^{-1} indicates that sulphur modification leads to blockage of the copper surface sites. Hence, this steric or geometric effect explains the marked decrease in hydrogenation activity of the Cu/Al_2O_3 catalyst following thiophene treatment.

The IR studies of thiophene adsorption on reduced Cu/Al_2O_3 catalyst demonstrate that thiophene is molecularly adsorbed at ambient temperature. Raising the temperature leads to a loss of the bands associated with molecularly adsorbed thiophene, indicating that the surface Cu–thiophene complex decomposes at the temperatures used in the catalytic studies. However, when the reduced Cu/Al_2O_3 catalyst was treated with thiophene at elevated temperatures no sulphur was detected in the effluent gas from the reactor, even though a sulphur-sensitive flame photometric detector (FPD) was used. Hence it is considered that the sulphur is retained on the copper surface, leading to the creation of Cu^0–S and Cu^+–S surface sites as characterised by infrared spectroscopy using CO as a probe molecule. Since electronic effects are known to be of short range (17, 18) it can be concluded that these Cu^+S sites must be in close proximity to the adsorbed sulphur atom. The amounts of sulphur required to achieve the marked effect on selectivity are low. Effects are observed with 0.1 μl thiophene/0.1 g catalyst, although the most pronounced effects are observed with 1 μl thiophene/0.1 g catalyst. Experiments using on-line sulphur-sensitive FPD showed that ca. 80% of an initial injection of 1 μl thiophene was retained on the catalyst and that subsequent 1 μl thiophene injection did not significantly enhance the amount of sulphur adsorbed. These levels of sulphur are therefore considered to be sufficient to form the new Cu^0–S and Cu^+–S surface sites.

It is necessary to consider whether the enhanced selectivity to the unsaturated alcohol is due to a purely steric effect induced by the new Cu^0–S or Cu^+–S surface sites or whether electronic factors are also important. For the Cu^0–S sites, these can be considered to be sterically hindered Cu^0 sites that were present prior to thiophene treatment whereas the Cu^+–S sites are found only after exposure to thiophene. In this study it has been shown that ca. 80% of 1 μl thiophene is retained on the Cu/Al_2O_3 catalyst following pretreatment, i.e., 6.1×10^{17} atoms of sulphur. The copper surface areas of the catalysts used in this study are in the range 15-22 m^2g^{-1} (10), i.e. 2.3×10^{20}–3.4×10^{20} surface copper atoms. On this basis, if it is assumed that all of the sulphur is adsorbed on the copper surface, the ratio of surface atoms S/Cu = 1.8–2.7×10^{-3}. Joyner and Pendry (18) indicated that the maximum range over which sulphur can act as a poison on supported metal catalysts is at a radius of 7 Å, but it normally is expected to act at a range of 5 Å. Hence, for the range of copper surface areas observed, the adsorbed sulphur can be expected to affect 3–8% of the available copper surface. On this basis it appears unlikely that a steric effect alone is responsible for the observed effects. Further evidence to discount a steric effect can be observed from the experimental data, since if a purely steric effect were responsible for the enhancement in unsaturated alcohol selectivity, then it could be expected that the overall yield of the unsaturated alcohol would not be affected by thiophene. This would result from the consideration that the activity of the Cu^0 sites would not be enhanced by steric hindrance. In this case, it would be expected that thiophene treatment would lead to a decrease in the hydrogenation rate of the α,β-unsaturated compound but that the overall rate of formation of the unsaturated alcohol would remain largely unchanged. This is not observed since thiophene treatment of the Cu/Al_2O_3 gives an enhancement in the rate of unsaturated alcohol formation. Furthermore, the steric hindrance effect would be expected to be more marked for crotonaldehyde when compared to acrolein. However, this is not the case, since the enhancement in rate of formation of allyl alcohol from acrolein is significantly higher than the enhancement in crotyl alcohol formation from crotonaldehyde (see Table 4). We therefore conclude that the main promotional effect of sulphur modification of copper catalysts is electronic in nature and on this basis it is the creation of the new Cu^+–S sites that leads to the enhancement in the formation of the unsaturated alcohols.

The results of this detailed study indicate that sulphur modification of Cu/Al_2O_3 catalyst, using thiophene as the source of sulphur, leads to a promotion in the rate of formation of the unsaturated alcohol from hydrogenation of an α,β-unsaturated aldehyde. The observed maximum selectivities to unsaturated alcohols are much higher than those observed in previous studies (1–6), and it is clear that this study demonstrates that partial catalyst poisoning represents a viable research approach to control reaction selectivity.

ACKNOWLEDGMENTS

We thank the SERC Interfaces and Catalysis Initiative and ICI Katalco for financial support.

REFERENCES

1. Noller, H., and Germain, J. E., *J. Catal.* **85,** 25 (1984).
2. Vannice, M. A., and Sen, B., *J. Catal.* **115,** 65 (1989).
3. Somonik, J., and Beranek, P., *Collect. Czech. Chem. Commun.* **37,** 353 (1972).
4. Bonnelle, T. R., Hubaut, R., and Daage, M., *Appl. Catal.* **22,** 231 (1986).
5. Waghray, A., Wang, J., Ouckaci, R., and Blackmond, D. G., *J. Phys. Chem.* **96,** 5954 (1992); *Catal. Lett.* **14,** 114 (1992).
6. Marinelli, T. B. L. W., Vleeming, J. H., and Ponec, V., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, P. Tétényi, and F. Solymosi, Eds.), p. 1211. Akadémiai Kiadó, Budapest, 1993.
7. Twigg, M.V., "Catalyst Handbook." Wolfe, Frome, England, 1989.
8. Bartholomew, C. H., Agrawal, P. K., and Katzer, J. R. *Adv. Catal.* **31,** 135 (1982).
9. Sterba, M. J. and Haensel, V., *Ind. Eng. Chem. Prod. Res. Dev.* **15** 2 (1976).
10. Hutchings, G. J., King, F., Okoye, I. P., and Rochester, C. H., *Appl. Catal.* **83,** L7 (1992).
11. Padley, M. B., Rochester, C. H., Hutchings, G. J., and King, F., *J. Catal.* **148,** 438 (1994).
12. Sexton, B. A., *Surf. Sci.* **163,** 99 (1985).
13. Lokhov, Y. A., and Davydov, A. A., *Kinet. Katal.* **20,** 1498 (1979).
14. Fu, Y., Tain, Y., and Lin, P., *J. Catal.* **132,** 85 (1991).
15. Hiere, R., Urbach, H.-P., Knözinger, H., *J. Chem. Soc. Faraday Trans. 1* **88,** 255 (1992).
16. Oudar, J., *Catal. Rev.-Sci. Eng.* **22,** 171 (1980).
17. Maclaren, J. M., Vvedensky, D. D., Pendry, J. B., and Joyner, R. W., *J. Chem. Soc. Faraday Trans. 1* **83,** 1945 (1987).
18. Joyner, R. W., and Pendry, J., *Catal. Lett.* **1,** 1 (1988).
19. Toolenaar, F. J. C. M., Stoop, F., and Ponec, V., *J. Catal.* **82,** 1 (1983).