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Modification of Selectivity in the Hydrogenation of Crotonaldehyde Using Cu/Al_2O_3 Catalysts Modified with Sulphur Compounds: Effect of Sulphur Source

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The hydrogenation of the α,β-unsaturated aldehyde crotonaldehyde has been studied over 5% Cu/Al_2O_3 and sulphur-modified 5% Cu/Al_2O_3 catalysts. The range of sulphur compounds included thiophene, thiophane, DMSO, DMS, SO_2, and CS_2. Following modification, an increase in the selectivity to the unsaturated alcohol, crotyl alcohol, was observed, and although the magnitude of this effect depended on the sulphur compound, the selectivity enhancement is concluded to be a general effect for supported copper catalysts modified by sulphur compounds. The enhancement in selectivity to crotyl alcohol decreases in the following order: thiophene > DMSO ~ thiophane ~ DMS > SO_2 ~ CS_2 for catalysts examined at constant temperature and crotonaldehyde conversion. The catalytic observations are combined with the results of FTIR spectroscopic characterisation of modified and unmodified Cu/Al_2O_3 using carbon monoxide as a probe molecule. The origin of the effect is discussed in terms of the formation of modified Cu^0 and Cu^+ surface sites. © 1994 Academic Press, Inc.

INTRODUCTION

The control of selectivity in the hydrogenation of α,β-unsaturated aldehydes is a problem that is frequently encountered in the production of fine chemicals for the pharmaceutical and food industries. A number of these hydrogenations are carried out using stoichiometric homogeneous hydrogenation, and to date heterogeneous catalytic reactions have proved less successful. However, a number of studies have been made concerning control of selectivity for the hydrogenation of crotonaldehyde to crotyl alcohol with Ni–Cu/Al_2O_3 (1), Pt/TiO_2 (2), Pt–Fe/SiO_2 (3), and Cu/Cr_2O_3 (4). In addition some studies have considered the use of catalyst promoters to influence selectivity. For example, Marinelli *et al.* (5) found an enhancement in the selectivity of allyl alcohol formation from acrolein when oxides of Ge, Ga, and Sn were added to supported Pt catalysts. Also, the addition of potassium to supported ruthenium catalysts (6) has been shown to result in a marked change in product selectivity for the hydrogenation of 3-methylbut-2-enal. Recently, we have shown (7, 8) that partial poisoning of supported copper catalysts with sulphur compounds enhances the rate of formation of the unsaturated alcohol from the hydrogenation of the unsaturated aldehyde. In these studies thiophene was used as the sulphur source and it was found that the thiophene decomposed to create Cu^0–S and Cu^+–S surface sites which were associated with the promotion in selectivity. In this study, a range of sulphur sources is investigated as partial catalyst poisons to determine whether the selectivity enhancement is a general effect for sulphur modification of supported copper catalysts.

EXPERIMENTAL

The catalyst, 5% Cu/Al_2O_3 (0.1 g), prepared as previously described (7, 8), was reduced *in situ* in hydrogen (3.6 liter h^{-1}) at 210°C for 16 h. Crotonaldehyde was fed to the reactor using a calibrated syringe pump and vaporised in a preheated reactor inlet zone. Hydrogen was used as both reactant and carrier gas, and the H_2 : crotonaldehyde ratio was 14 : 1 in all experiments. Modified catalysts were prepared by injection of either liquid or gaseous sulphur compound 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 error associated with the conversion and selectivity data reported in this paper is < ±1%. The infrared studies were conducted using self-supported catalyst discs using a method previously described (8).

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RESULTS

Comparison of Sulphur Poisons

The effect of reaction temperature on the hydrogenation of crotonaldehyde over 5% Cu/Al_2O_3 in the presence and absence of SO_2 and CS_2 is shown in Table 1. The three possible hydrogenation products: crotyl alcohol, butanal, and 1-butanol are observed together with the products of condensation reactions not involving hydrogenation. In the absence of a sulphur compound, conversion increases rapidly with temperature and the selectivity to 1-butanol similarly increases. Pretreatment with SO_2 (0.1 ml/0.1 g catalyst, 150°C) does not significantly influence the catalyst performance at 100°C. However, at 150°C, SO_2 does lead to a marked decrease in conversion as would be expected from the known effect of sulphur compounds as a poison for copper catalysts (9, 10). In addition, the selectivity to crotyl alcohol is enhanced compared to the untreated catalyst under identical conditions. Similar but less marked effects were observed for pretreatment with CS_2 (0.3 μl CS_2/0.1 g catalyst, 150°C).

It is apparent that modified catalysts demonstrate decay in crotonaldehyde conversion with increased reaction time (Table 1), and this effect for a range of sulphur poisons is shown in Fig. 1. In the absence of the sulphur poison, no loss of conversion is observed for this reaction condition. However, in the presence of sulphur compound a rapid deactivation is observed in the initial 30–60 min, but after this time relatively stable catalyst performance is attained. In general, the selectivity to crotyl alcohol increases with increased time-on-line, and the selectivity to 1-butanol is decreased. Representative data in the presence and absence of SO_2 (0.2 ml/0.1 g catalyst) are shown in Fig. 2.

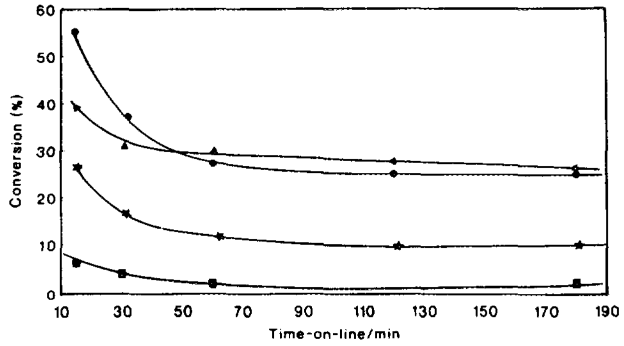

FIG. 1. Effect of time-on-line on crotonaldehyde conversion over 5% Cu/Al_2O_3 for different sulphur poisons: (●) thiophene (1 μl); (▲) DMSO (1 μl); (*) SO_2 (0.2 μl); (■) CS_2 (1 μl). Catalyst pretreated at 210°C; reaction temperature = 150°C; WHSV = 1.2 h^{-1} (untreated catalyst 100% conversion at all times).

The effect of the temperature of treatment with a sulphur compound on the conversion and the product selectivity are shown in Figs. 3 and 4, respectively, for a range of sulphur poisons. The poisoning effects of SO_2 and CS_2 show similar trends, and they have a most marked effect at low temperatures of treatment, whereas thiophene and DMSO have the more marked effects at much higher temperatures of treatment. For CS_2 treatment at 25°C, a marked enhancement in the selectivity to crotyl alcohol was observed. Comparison of results at similar conversions and constant temperature for treated and untreated catalysts (Fig. 5) indicates that the enhancement in crotyl alcohol selectivity is not related solely to decreased con-

TABLE 1

Effect of SO_2 and CS_2 Addition on the Hydrogenation of Crontonaldehyde over Cu/Al_2O_3[a]

		Sulphur compound														
		None					SO_2[b]					CS_2[c]				
			Selectivity (%)					Selectivity (%)					Selectivity (%)			
Temp. (°C)	Time-on-line (min)	Conv. (%)	Crotyl alcohol	Butanal	Butanol	Other[d]	Conv. (%)	Crotyl alcohol	Butanal	Butanol	Other[d]	Conv. (%)	Crotyl alcohol	Butanal	Butanol	Other[d]
100	15	15.7	7	83	7	3	15.4	10	74	13	3	14.0	11	71	16	2
	30	14.1	13	83	—	4						11.0	10	85	3	2
	60	15.8	9	87	—	4	12.3	12	86	—	2	10.3	9	87	—	4
	120	14.1	8	88	—	4	11.9	10	87	—	3	10.2	12	84	—	4
	180	15.5	12	86	—	3	11.3	9	87	—	4	9.9	9	86	—	5
150	15	100	1	0.3	95	3.7	42.3	5	78	15	2	100	1	8	89	2
	30	100	1	1	98	—	33.6	9	83	5	3	99.4	1	41	58	—
	60	100	1	22	77	—	28.4	9	83	4	4	88.9	4	63	33	—
	120	100	1	49	50	—	27.6	11	82	2	5	89.4	4	66	30	—
	180	100	2	55	43	—	26.3	12	79	2	7	75.9	6	73	23	—

[a] 5% Cu/Al_2O_3 reduced at 210°C; crotonaldehyde WHSV = 1.2 h^{-1}; H_2 : crotonaldehyde = 14 : 1.

[b] SO_2, 0.1 ml/0.1 g catalyst, 150°C.

[c] CS_2, 0.3 μl/0.1 g catalyst, 150°C.

[d] Condensation by-products.

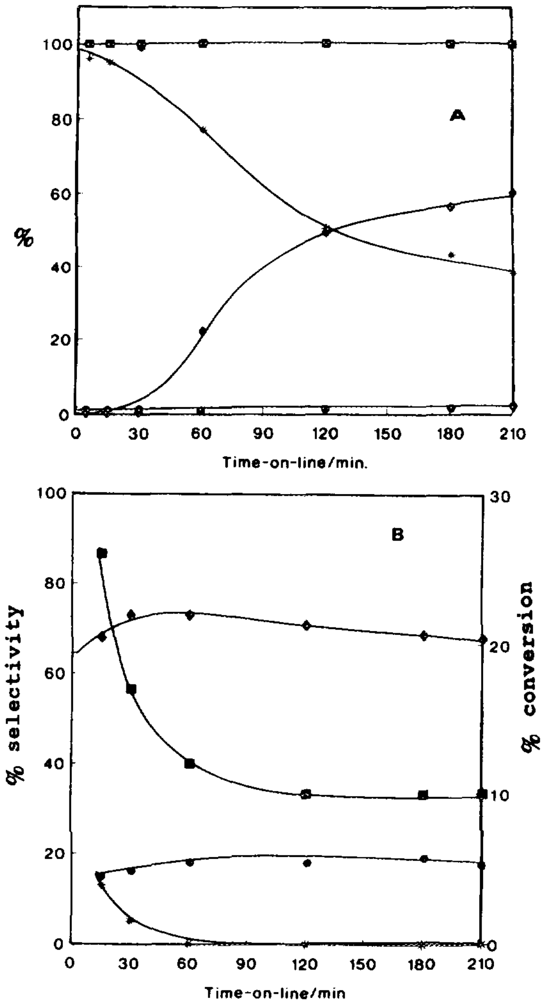

FIG. 2. Effect of time-on-line on performance of 5% Cu/Al$_2$O$_3$: (A) unmodified and (B) modified with 0.2 ml SO$_2$/0.1 g catalyst at 150°C. Reaction temperature = 150°C; WHSV = 1.2 h^{-1}: (●) crotyl alcohol; (◆) butanal; (*) butanol (■) crotonaldehyde conversion.

TABLE 2

Comparison of the Effect of Sulphur Poisons on the Selectivity of the Hydrogenation of Crotonaldehyde at 30% Conversion[a]

Sulphur	Amount/0.1 g catalyst	Product selectivity (%) Crotyl alcohol	Butanal	Butanol	Other[b]
Thiophene	1 μl	18	70	6	6
DMSO	1 μl	16	76	4	4
Thiophane	1 μl	15	76	6	3
DMS	1 μl	14	78	4	5
SO$_2$	0.1 μl	9	82	5	4
CS$_2$	0.2 μl	8	86	2	4
None	—	3.5	20.5	76	—

[a] 5% Cu/Al$_2$O$_3$ reduced 210°C, sulphided at 210°C; reaction temperature 150°C; H$_2$: crotonaldehyde = 14 : 1.

[b] Condensation by-product.

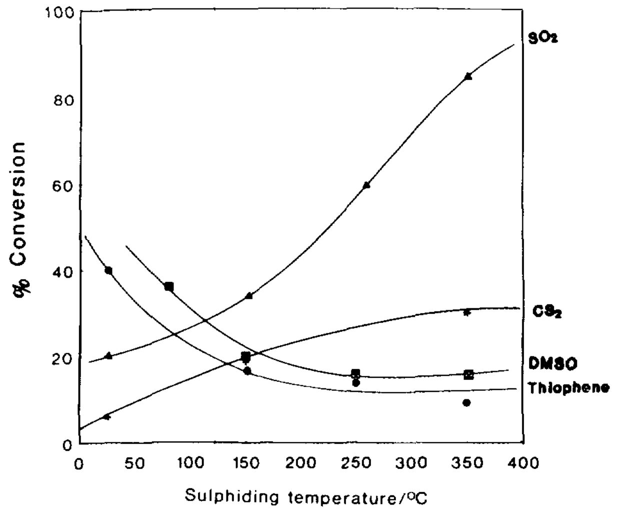

FIG. 3. Effect of treatment temperature on crotonaldehyde conversion over 5% Cu/Al$_2$O$_3$ at 150°C; 30 min time-on-line (untreated catalyst 100% conversion): (▲) SO$_2$ (0.1 ml); (*) CS$_2$ (0.3 μl); (■) DMSO (1 μl); (●) thiophene (1 μl).

version, and the most marked effects are for thiophene (Table 2).

The effect of the level of SO$_2$ is shown in Fig. 6 for modification of Cu/Al$_2$O$_3$ at 150°C. This temperature was selected since the unmodified 5% Cu/Al$_2$O$_3$ catalyst was found to demonstrate low selectivity to crotyl alcohol. Increasing the amount of SO$_2$ leads to an increase in crotyl alcohol selectivity, and crotonaldehyde conversion decreases markedly as does the selectivity to 1-butanol. At low levels of SO$_2$, the poisoning effect is most marked for butanal selectivity which is significantly enhanced. Similar effects are observed for the effect of the level of CS$_2$ on catalyst performance (Fig. 7).

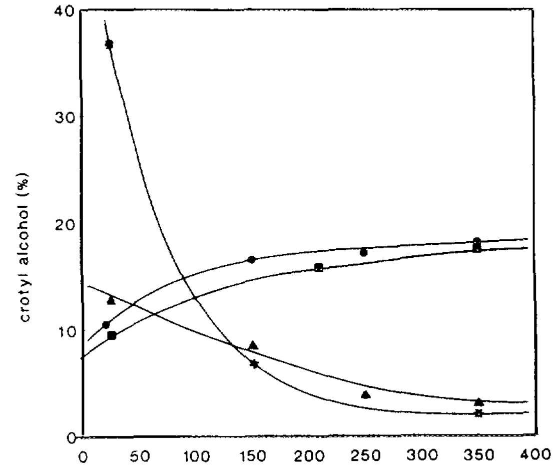

FIG. 4. Effect of treatment temperature on crotyl alcohol selectivity; conditions and key as for Fig. 3.

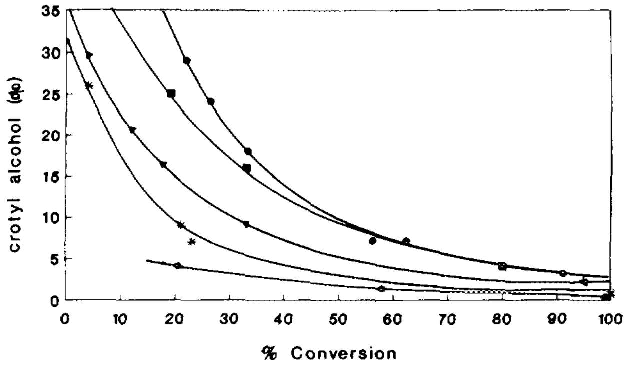

FIG. 5. Effect of sulphur poisons on crotyl alcohol selectivity; temperature of treatment = 210°C; reaction temperature = 150°C; 30 min time-on-line: (●) thiophene (1 μl); (■) DMSO (1 μl); (▲) SO_2 (0.1 ml); (*) CS_2 (0.2 μl), (◆) unsulphided.

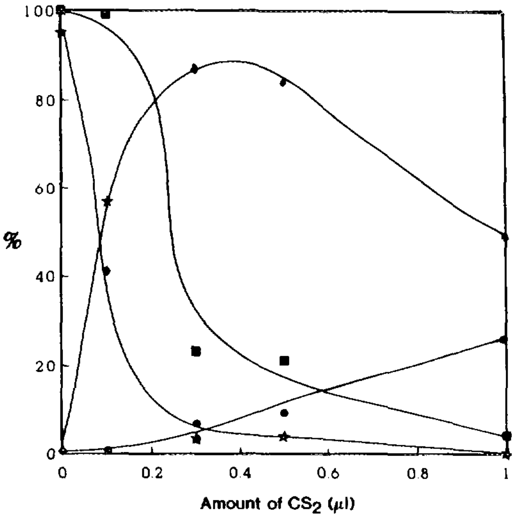

FIG. 7. Effect of amount of CS_2 on the hydrogenation of crotonaldehyde. Reaction conditions and key as for Fig. 6.

IR Characterisation of the Interaction of Sulphur Dioxide with 5% Cu/Al_2O_3

The effect of SO_2 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 catalyst was initially exposed to SO_2 (270 N m^{-2}) at ambient temperature for 5 min followed by flowing hydrogen (100 cm^3 min^{-1}) at the same temperature (Fig. 8). The band observed at 1065 cm^{-1} was characteristic of sulphite chemically adsorbed on unsaturated Al^{3+} sites (11). In addition, bands appearing at 1330 and 1150 cm^{-1} were assigned to vibrations of SO_2 physically adsorbed on surface hydroxyl groups (12). In a separate experiment (13), these bands were also absent under identical conditions for SO_2 adsorption on the alumina alone in the absence of copper. These bands are therefore assigned to interactions of SO_2 with the support. No IR bands were observed which might be assigned to the interaction of SO_2 with the reduced copper surface. However, coadsorption studies with CO demonstrate that SO_2 intereacts irreversibly with the reduced copper surface (13). Leung *et al.* (14), in an EELS study, found evidence that the dissociation of SO_2 at 27°C on a copper surface generated an oxygen-bound sulphite species which gave a band below 1000 cm^{-1} which would not be detectable in the present study.

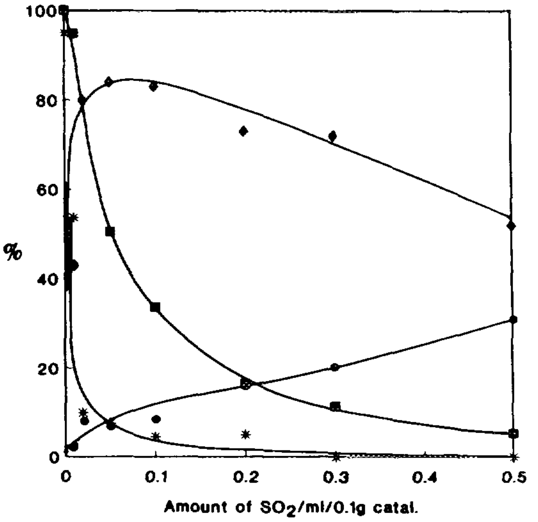

FIG. 6. Effect of amount of SO_2 on the hydrogenation of crotonaldehyde, catalyst treated at 150°C; reaction temperature = 150°C; WHSV = 1.2 h^{-1}; 30 min time-on-line: (●) crotyl alcohol selectivity; (◆) butanal selectivity; (*) butanol selectivity; (■) conversion.

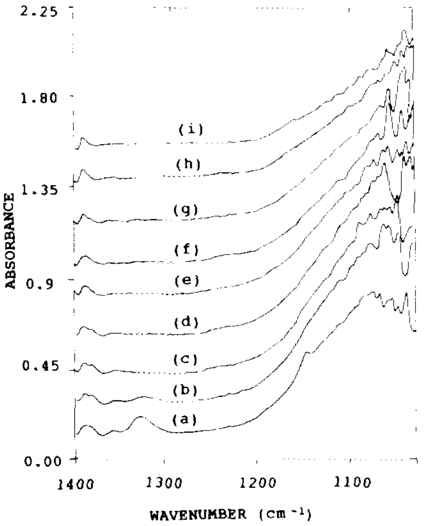

FIG. 8. Reduced Cu/Al_2O_3, exposed to (a) 270 Pa SO_2 (5 min) followed by flowing H_2 (100 cm^3 min^{-1}) at (b) ambient temperature, (c) 50, (d) 70, (e) 100, (f) 120, (g) 150, (h) 170, and (i) 200°C, each sample equilibrated for 10 min.

The temperature was increased in 25°C increments to 200°C (Fig. 8) under the hydrogen flow. The intensities of the bands at 1330 and 1150 cm^{-1}, due to physically adsorbed SO_2 species, declined to zero by 50°C. In addition increasing the temperature to 200°C resulted in a reduction in the intensities of vibrations due to chemically adsorbed sulphur species on the alumina surface (Fig. 8). Identical behaviour was noted in the absence of reduced copper. No additional bands appeared which could be assigned to the interaction of SO_2 with the reduced copper surface.

The sample was then evacuated and cooled to ambient temperature before admission of CO. Addition of CO resulted in the appearance of a ν(CO) band envelope at 2129, 2116(sh), and 2099(sh) cm^{-1} (Fig. 9). The intensity of this band envelope was more than an order of magnitude less than that observed in a similar experiment in the absence of SO_2 (8). As discussed previously (8), bands in the region of 2116 (sh) and 2129 cm^{-1} are indicative of CO bound to copper(I) sites, and that at 2099 cm^{-1} is characteristic of Cu^0–CO species. The IR experiments as a whole indicate that there are a number of surface sites present on the SO_2-treated Cu/Al_2O_3 catalyst in which Cu^0 and Cu^+ are located in close proximity to adsorbed sulphur species.

DISCUSSION

The results of this study indicate that modification of Cu/Al_2O_3 catalyst by sulphur compounds can give marked and sustained activity and selectivity effects in the hydrogenation of the α,β-unsaturated aldehyde crotonaldehyde. A range of sulphur compounds have been investigated, namely, thiophene, thiophane, DMSO, DMS, SO_2, and CS_2, and all result in an overall loss in hydrogenation activity with concomitant increase in the selectivity to the partial hydrogenation products butanal and crotyl alcohol, although the degree of these effects is dependent on the nature of the sulphur source. Analysis using a sulphur-sensitive flame photometric detector during catalyst treatment with sulphur compounds indicated that 80–90% of the sulphur component was adsorbed, and that no sulphur was eluted from the catalyst during the subsequent hydrogenation reaction, indicating that the sulphur is retained on the catalyst. Experiments conducted with approximately similar levels of added sulphur (4×10^{-4} g/0.1 g catalyst) at 210°C show that the effect on crotonaldehyde conversion at 150°C, 1.2 h^{-1} decreases in order

$$\text{DMSO} \approx \text{thiophene} > CS_2 > SO_2,$$

whereas for treatment at 25°C the conversion at 150°C decreases in order

$$CS_2 > SO_2 > \text{thiophene} > \text{DMSO}.$$

This effect of temperature may be related to enhanced adsorption of CS_2 and SO_2 at 25°C since thiophene and DMSO would be strongly adsorbed at both temperatures investigated. At 25°C, it can be expected that thiophene and DMSO are molecularly adsorbed. Infrared studies with thiophene have confirmed that this is the case (8). At higher temperatures, e.g., 150°C, both thiophene and DMSO will decompose to give a surface modified by sulphur species and hence this may account for the different temperature effects observed.

Modification of the Cu/Al_2O_3 catalyst by sulphur compounds leads to a catalyst that preferentially hydrogenates the carbonyl bond rather than the carbon–carbon double bond, which is more readily hydrogenated in the absence of sulphur. For equivalent amounts of sulphur, this effect is most marked for thiophene when catalysts are compared at constant conversion and temperature with CS_2 and SO_2 giving the lowest enhancement in selectivity.

Use of CO as a probe molecule following catalyst treatment with sulphur compounds is instructive. When the catalyst is treated with SO_2, a marked decrease is observed in the intensity of the CO stretching band envelope at 2200–2100 cm^{-1}, indicating that sulphur modification leads to blockage of the surface copper sites. Similar results have been observed in our previous studies with thiophene (8). Hence this steric or geometric effect explains the marked decrease in hydrogenation activity of the Cu/Al_2O_3 catalyst following modification.

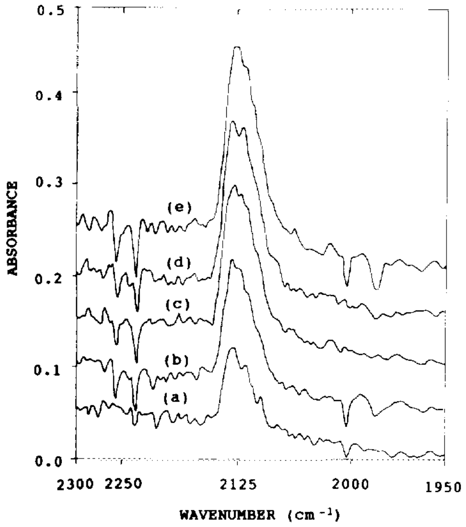

FIG. 9. Reduced Cu/Al_2O_3 exposed to 270 Pa SO_2 and flowing H_2 at 200°C followed by evacuation and cooling to ambient temperature. Sample then exposed to (a) 0.27, (b) 0.53, (c) 0.80, (d) 1.06, and (e) 1.33 kPa CO at ambient temperature.

The IR studies of SO_2 adsorption on reduced Cu/Al_2O_3 catalyst demonstrate that SO_2 is adsorbed at ambient temperature and raising the temperature leads to a loss of the bands associated with this adsorbed species. However, when the reduced Cu/Al_2O_3 catalyst was modified at elevated temperatures, no sulphur was detected in the reactor effluent gases. Hence it is concluded that sulphur species are retained on the surface leading to the creation of Cu^0–S and Cu^+–S sites as characterised by infrared spectroscopy using CO as a probe molecule. Similar findings were observed when the Cu/Al_2O_3 catalyst was pretreated with thiophene (8). It is therefore clear that the sulphur compound decomposes on the surface to give an adsorbed sulphur species and that this process occurs for the broad range of sulphur compounds studied. There exist clear similarities between the observed effects of pretreatment with thiophene or SO_2, i.e., both lead to a similar reduction in intensity of the ν_{CO} band under identical conditions, and both result in the production of Cu^+–S and Cu^0–S sites. However, there are differences in the catalytic performance of the two modified surfaces. The thiophene-pretreated catalyst exhibits higher selectivity to crotyl alcohol when compared to the SO_2-pretreated catalyst at the same crotonaldehyde conversion and temperature. There are also differences in the ν_{CO} band envelope for CO adsorbed on these surfaces (Fig. 10), and these differences may be related to the observed selectivity differences. In particular, the thiophene-treated catalyst appears to be more metallic in nature and, as expected, the SO_2-treated Cu/Al_2O_3 more oxidised. This indicates that different distributions of the Cu^0–S and Cu^+–S sites exist on these two surfaces. In addition, the hydrocarbon fragment from the decomposition of thiophene may also play an important role in structuring the active surface, and this may account for some differences in the reactivity observed, which is an aspect requiring further study.

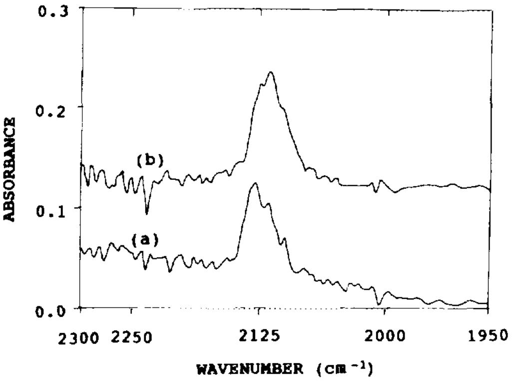

FIG. 10. (a) Reduced Cu/Al_2O_3 exposed to 270 Pa SO_2 and flowing H_2 at 200°C followed by evacuation and cooling and exposure to 0.27 kPa CO at ambient temperature. (b) Reduced Cu/Al_2O_3 treated as in (a) but with 1.33 kPa thiophene (rather than SO_2).

The results of this study indicate that sulphur modification of Cu/Al_2O_3 catalyst leads to sustained reactivity effects in the hydrogenation of the α,β-unsaturated aldehyde crotonaldehyde. In particular, modification by sulphur compounds creates Cu^0–S and Cu^+–S surface sites that are more selective for the hydrogenation of the carbonyl bond in preference to the carbon–carbon double bond. Although there are differences concerning the magnitude of this effect, it is observed with a broad range of sulphur compounds. In addition, we have previously shown (8) that the effect is also broadly independent of the support used for the copper. Hence, we conclude that the observed effects are a general feature of copper catalysts and are of relevance to supported metal catalysts in general. This study further confirms our view (8) that partial catalyst poisoning represents a viable research approach to controlling reaction selectivity.

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