

# Effects of thiophene and SO<sub>2</sub> on acrolein hydrogenation over Co/SiO<sub>2</sub> catalysts

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## Abstract

Infrared spectra are reported of adsorbed species and gaseous products in the reactions over SO<sub>2</sub>-modified Co/SiO<sub>2</sub> of acrolein, propanal, allyl alcohol and propan-1-ol with and without hydrogen. Low coordination edge or step sites in high index planes contain Co<sup>n+</sup> Co<sup>o</sup> sites which are active for C=O hydrogenation but are completely poisoned by SO<sub>2</sub> pretreatment. Formation of 2-methylpenten-2-al from propanal by an aldol reaction over oxidic cobalt sites was promoted by SO<sub>2</sub> but inhibited by hydrogen. Low index planes contain Co<sup>o</sup> sites which are available for C=C hydrogenation of acrolein but are inactive for allyl alcohol hydrogenation because of strong chemisorption of allyl alcohol on the SO<sub>2</sub>-treated surface. Propanol was the dominant product from acrolein, propanal and allyl alcohol hydrogenation over unmodified Co/SiO<sub>2</sub> but was not formed over SO<sub>2</sub> modified catalyst. The acrolein reaction gave propanal alone. Thiophene caused partial poisoning of both low coordination and high coordination sites on Co/SiO<sub>2</sub>, the hydrogenation of acrolein giving propanal and propan-1-ol but at lower rates than for unmodified Co/SiO<sub>2</sub>. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Acrolein hydrogenation; Sulphur dioxide poisoning; Thiophene poisoning; Supported cobalt catalyst

## 1. Introduction

The modification and poisoning of cobalt surface sites in Co/SiO<sub>2</sub> catalyst by thiophene and sulphur dioxide has been characterised by competitive experiments involving infrared spectroscopic study of CO adsorption [1]. Both cationic cobalt sites (Co<sup>3+</sup> and Co<sup>2+</sup>) and at least three types of Co<sup>o</sup> site existed in reduced catalyst. The different sites were differently af-

ected by the adsorption of thiophene or sulphur dioxide. The pretreatment of Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/SiO<sub>2</sub> with thiophene and of Cu/Al<sub>2</sub>O<sub>3</sub> with sulphur dioxide enhanced catalyst selectivity to crotyl alcohol in the hydrogenation of crotonaldehyde [2,3] although only a small enhancement in allyl alcohol formation has been reported in similar studies of acrolein hydrogenation [4]. The selectivity enhancement was attributed to the coexistence on the modified copper surface of both cationic and Cu<sup>o</sup> sites which jointly activated C=O bond hydrogenation. Despite containing both cationic Co and Co<sup>o</sup> sites, the reduced Co/SiO<sub>2</sub> characterised

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by CO adsorption [1] converted acrolein in hydrogen to propanal and subsequently propan-1-ol with no evidence for allyl alcohol either as a product or as an adsorbed intermediate [5]. The present study was designed to test whether thiophene or sulphur dioxide modification of Co/SiO<sub>2</sub> would promote selectivity towards allyl alcohol in acrolein hydrogenation. Specific concern was with identifying adsorbed species present during reaction and correlating these with the appearance of specific products.

## 2. Experimental

Reduced catalyst containing 5 wt.% Co was prepared from cobalt(II) nitrate dispersed on Cab-o-Sil silica (200 m<sup>2</sup> g<sup>-1</sup>) which was calcined for 1 h in flowing air at 673 K (giving Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>), evacuated (673 K, 40 min), cooled to 423 K in vacuum, and then reduced in a flow of hydrogen (1 atm, 150 cm<sup>3</sup> min<sup>-1</sup>) while the temperature was raised to 723 K over 3 h and then kept at 723 K for 15 h before

evacuation (723 K, 1 h) and subsequent cooling in vacuum to reaction temperature (373 K). In general catalyst was then exposed to modifier (thiophene or sulphur dioxide) at 373 K, before evacuation (1 min, 373 K) and admission of reactant (acrolein, allyl alcohol, propanal or propan-1-ol) with or without hydrogen. Self-supporting discs, for transmission spectroscopy using a Perkin-Elmer 1750 FTIR spectrometer at 4 cm<sup>-1</sup> resolution, were pressed from dried (air, 383 K, 16 h) catalyst precursor and mounted in the infrared cell before the calcination and reduction procedures.

Products of reaction were condensed at 77 K in a small cell which allowed analysis of the vapour phase by FTIR or mass spectrometry.

## 3. Results

### 3.1. Adsorption after sulphur dioxide pretreatment

Adsorption of SO<sub>2</sub> followed by evacuation left no adsorbed species on Co/SiO<sub>2</sub> which

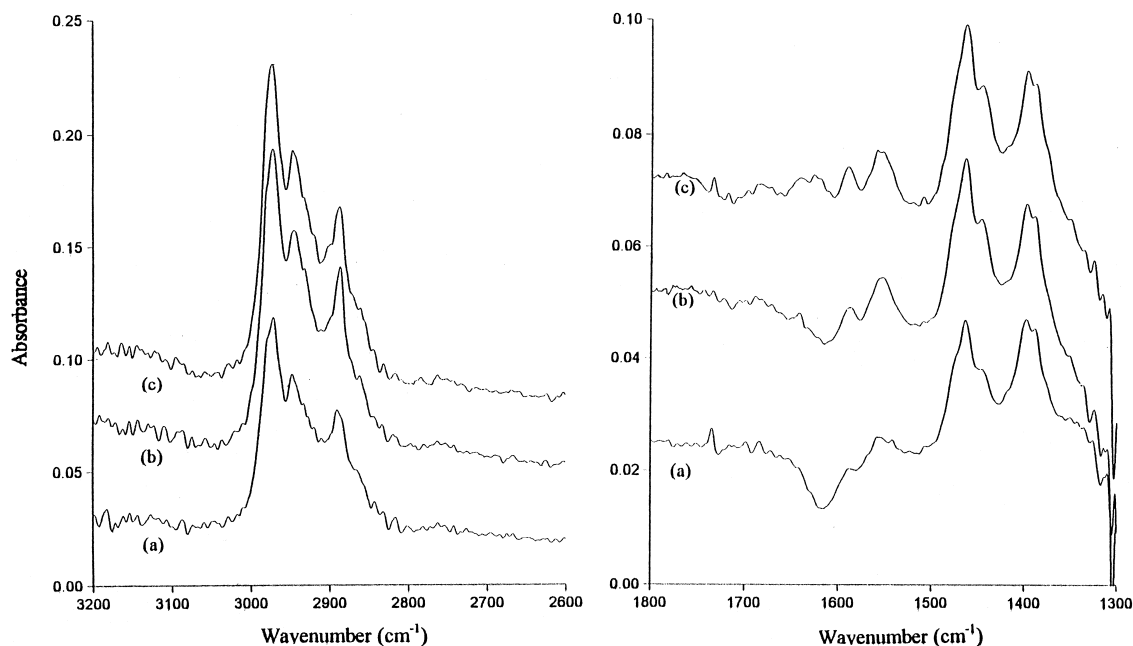


Fig. 1. Spectra of Co/SiO<sub>2</sub> at 373 K after exposure to SO<sub>2</sub> (6.7 N m<sup>-2</sup>, 10 min, 373 K), evacuation (1 min, 373 K) and exposure to propan-1-ol (28 N m<sup>-2</sup>, 373 K) for (a) 5 s, (b) 1 h, (c) 2 h.

could be detected in the infrared spectral range 4000–1300  $\text{cm}^{-1}$ . Exposure to propan-1-ol gave dominant bands at 2971, 2946, 2889, 1462 and 1398  $\text{cm}^{-1}$  (Fig. 1) which may be assigned to  $\nu_{\text{CH}}$  and  $\delta_{\text{CH}}$  vibrations of surface propoxy groups mainly on silica [5] with some on cobalt. Additional bands at 1446 and 1387  $\text{cm}^{-1}$  also suggest that adsorbed species were formed on cobalt. This was confirmed by weak bands at 1590 and 1560  $\text{cm}^{-1}$  which may be attributed to  $\nu_{\text{as}}$  vibrations of two forms of surface carboxylate. The low level of adsorption of propanol on  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  confirms the conclusion from experiments involving CO adsorption [1] that the cobalt surface was largely poisoned by  $\text{SO}_2$ . The condensed gas-phase gave a spectrum characteristic of propan-1-ol but also included weak maxima at 1762, 1745 and 1732  $\text{cm}^{-1}$  which were due to  $\nu_{\text{C=O}}$  vibrations of propanal with a relatively small amount of acrolein. Very weak bands at ca. 1600–1650  $\text{cm}^{-1}$  after prolonged contact (Fig. 1c) showed that adsorbed species, possibly acrylate or acrolein [6] containing alkenyl groups were also being formed.

Allyl alcohol adsorption under the standard conditions (Fig. 1) used for all adsorbates gave bands at 3090, 1468 and 1427  $\text{cm}^{-1}$  due to alkoxy groups mainly on silica but in part on cobalt. In addition, bands at 1642 ( $\nu_{\text{C=C}}$ ), 1553 ( $\nu_{\text{as}} \text{COO}^-$ ), 1441 ( $\nu_{\text{s}} \text{COO}^-$ ) and 1376  $\text{cm}^{-1}$  ( $\delta_{\text{CH}}$ ) (Fig. 2) may be attributed predominantly to surface acrylate possibly with a little propanoate which would have also contributed to the band at 1468  $\text{cm}^{-1}$ . A maximum at 1669  $\text{cm}^{-1}$  is typical of acrolein O-ligated [5] to  $\text{Co}^{n+}$  surface sites [1]. All the bands due to adsorbed alkoxy, acrylate, propanoate or acrolein on cobalt were weak confirming the general poisoning effect of  $\text{SO}_2$  pretreatment. The gas phase contained largely allyl alcohol but two medium intensity bands at 1732 and 1713  $\text{cm}^{-1}$  showed that acrolein was a significant product. A weak shoulder at 1762  $\text{cm}^{-1}$  suggested some propanal was also formed. The spectra of adsorbed species suggested that allyl alcohol

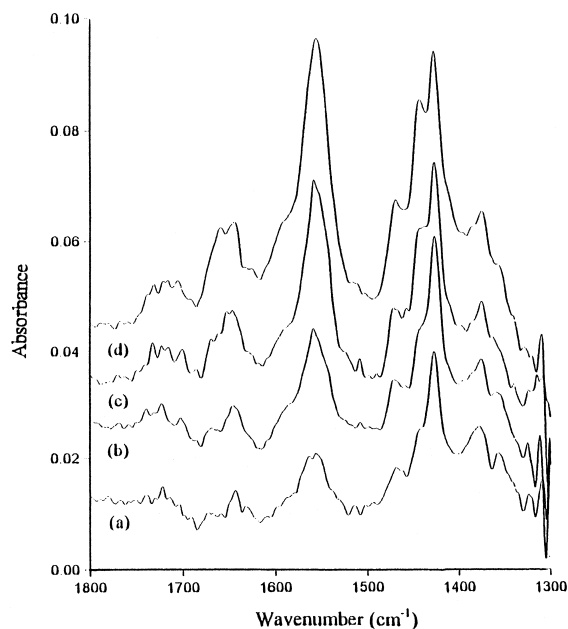


Fig. 2. As for Fig. 1 except exposure to allyl alcohol for (a) 5 s, (b) 10 min, (c) 1 h, (d) 2 h.

formed acrylate more readily than propan-1-ol formed propanoate on  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$ .

The adsorption of propanal on  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  at 373 K gave a band at 1679  $\text{cm}^{-1}$  due to propanal O-ligated to  $\text{Co}^{n+}$  sites and very weak bands in the range 1600–1350  $\text{cm}^{-1}$  which may be ascribed to surface propoxy and propanoate species which also gave characteristic bands at 3100–2800  $\text{cm}^{-1}$  (Fig. 3). The dominant band was at 1625  $\text{cm}^{-1}$ . Spectra of the gas phase showed that propanal was converted to a product giving a doublet at 1715 and 1706  $\text{cm}^{-1}$ . After 2 h the reaction was nearly complete and the condensed vapour gave a mass spectrum identical to that of 2-methyl-pent-2-enal, the formation of which by aldol condensation of propanal over  $\text{Co}/\text{SiO}_2$  has been reported before [7]. The band at 1625  $\text{cm}^{-1}$  is ascribed to  $\nu_{\text{C=C}}$  vibrations of an adsorbed intermediate in the formation of 2-methyl-pent-2-enal. The intermediate did not contain CHO groups which would have given a much stronger  $\nu_{\text{C=O}}$  band than the band due to  $\nu_{\text{C=C}}$  vibrations. However, in addition to the intense  $\nu_{\text{C=C}}$  band removal of the vapour phase by condensa-

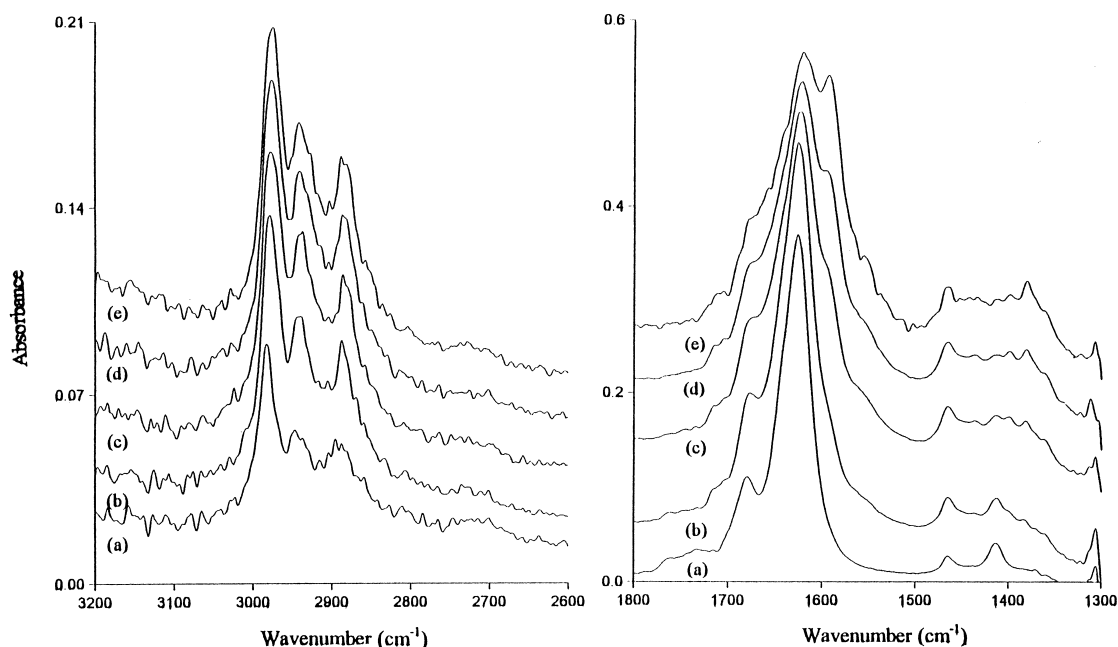


Fig. 3. As for Fig. 1 except exposure to propanal for (a) 5 s, (b) 10 min, (c) 30 min, (d) 1 h, (e) 2 h.

tion left weaker maxima at 1590, 1468, 1437 and 1384  $\text{cm}^{-1}$  which are ascribable [6] to surface alkyl or alkenyl carboxylate.

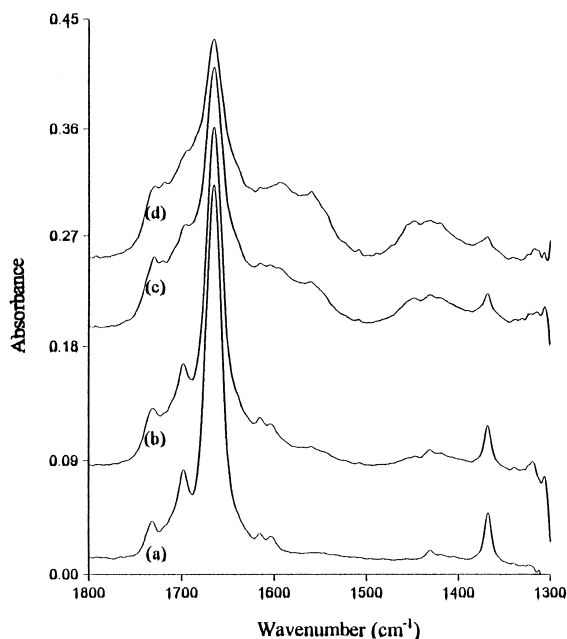


Fig. 4. As for Fig. 1 except exposure to acrolein for (a) 5 s, (b) 10 min, (c) 1 h, (d) 2 h.

Bands in spectra of acrolein adsorbed on  $\text{Co/SiO}_2$  (Fig. 4) were primarily due to  $\nu_{\text{C}=\text{O}}$  (1669, 1698  $\text{cm}^{-1}$ ) and  $\nu_{\text{C}=\text{C}}$  (1615, 1640  $\text{cm}^{-1}$ ) vibrations of acrolein ligated to cationic Co sites [1] by either O-ligation giving a  $\sigma$ -complex or C=C ligation giving a  $\pi$ -complex [5]. Bands at 1430 and 1368  $\text{cm}^{-1}$  were due to CH deformation vibrations of adsorbed acrolein and a maximum at 1732  $\text{cm}^{-1}$  was due to acrolein vapour. Subsequent growth of weak bands at 1559 and 1448  $\text{cm}^{-1}$  due to  $\nu_{\text{as}} \text{COO}^-$  and  $\nu_{\text{s}} \text{COO}^-$  vibrations of surface acrylate [5,6] showed that the adsorption of acrolein to give acrylate [5] had been heavily poisoned by  $\text{SO}_2$ -pretreatment. Acrylate was formed at the expense of the O-ligated  $\sigma$ -complex of acrolein responsible for an intense infrared band at 1669  $\text{cm}^{-1}$ . The condensed vapour phase gave a spectrum characteristic of acrolein alone.

### 3.2. Hydrogenation reactions after sulphur dioxide pretreatment

Simultaneous admission of allyl alcohol and hydrogen to  $\text{Co/SiO}_2$  (Fig. 5) did not give the

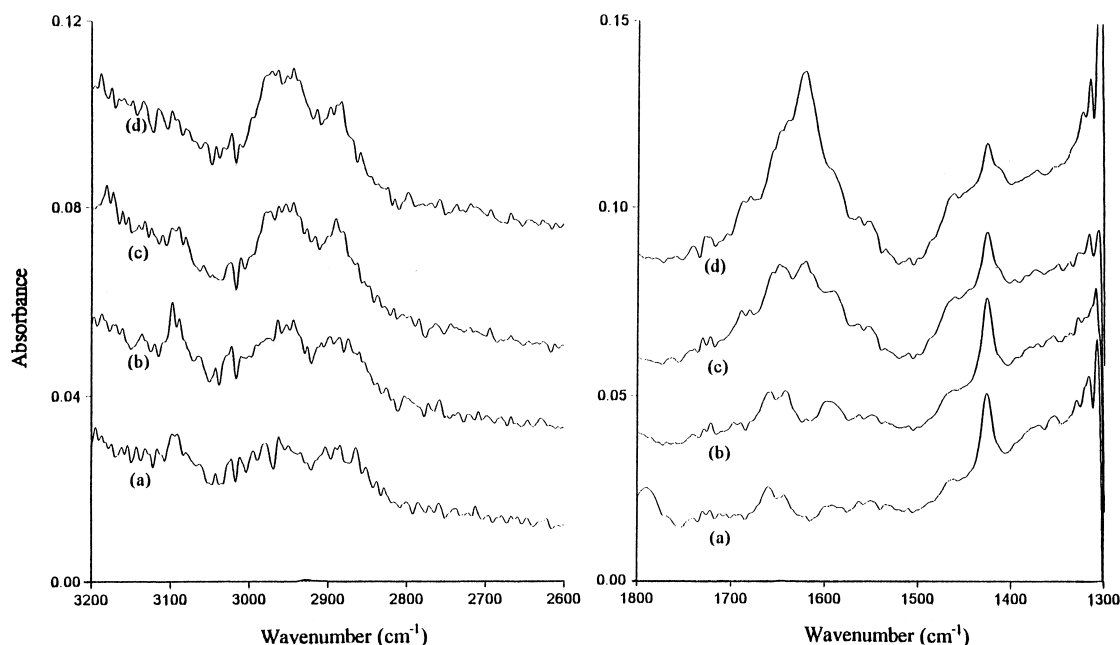


Fig. 5. Reduced Co/SiO<sub>2</sub> exposed to SO<sub>2</sub> (28 N m<sup>-2</sup>, 373 K, 10 min), evacuated (373 K, 1 min) and then exposed to an allyl alcohol (28 N m<sup>-2</sup>)/hydrogen (3.3 kN m<sup>-2</sup>) mixture at 373 K for (a) 10, (b) 30, (c) 90, (d) 120 min.

surface acrylate which was observed in the absence of hydrogen (Fig. 2). Furthermore, there were only very weak bands due to propanoate which might have arisen from acrylate hydrogenation. Bands at 3097, 1648 and 1426 cm<sup>-1</sup> were due to  $\nu_{\text{CH}}$ ,  $\nu_{\text{C}=\text{C}}$  and  $\delta_{\text{CH}}$  vibrations of alkoxy species, mainly on silica [5], but partly also on cobalt, which were slowly hydrogenated to give propoxy groups. A weak band at 1661 cm<sup>-1</sup> suggests the presence of acrolein  $\sigma$ -bonded to Co sites (Fig. 4). However, with time, a band became strong at 1625 cm<sup>-1</sup> (Fig. 5d) and coincided with the dominant maximum in spectra of propanal on SO<sub>2</sub>-treated Co/SiO<sub>2</sub>. Spectra of the vapour phase contained bands due to unreacted allyl alcohol and also 2-methylpent-2-enal. No propan-1-ol was formed in contrast to the result for Co/SiO<sub>2</sub> which had not been pretreated with SO<sub>2</sub> [5].

Spectra of Co/SiO<sub>2</sub> exposed to a propanal (28 N m<sup>-2</sup>)/hydrogen (3.3 kN m<sup>-2</sup>) mixture after pretreatment with SO<sub>2</sub> (28 N m<sup>-2</sup>, 373 K, 10 min) were nearly identical to the correspond-

ing spectra (Fig. 3) in the absence of hydrogen although all the bands were reduced ca. 33% in intensity. Similarly also, after 2 h reaction, the dominant product in the vapour phase was 2-methylpent-2-enal although more unreacted propanal remained than for propanal alone. The presence of hydrogen partially inhibited the aldol condensation reaction leading to 2-methylpent-2-enal. These results contrast with those for propanal/hydrogen over Co/SiO<sub>2</sub> which had not been pretreated with SO<sub>2</sub> where propanoate was the dominant adsorbed product and 2-methylpent-2-enal was not a detectable product, only propan-1-ol being formed [5]. No propan-1-ol was observed for propanal/hydrogen over SO<sub>2</sub>-treated Co/SiO<sub>2</sub>. Furthermore, there were no bands due to adsorbed CO on cobalt for Co/SiO<sub>2</sub> pretreated with SO<sub>2</sub>. Untreated Co/SiO<sub>2</sub> gave adsorbed CO resulting from decomposition of propanal in the presence of hydrogen [5].

The hydrogenation experiments involving allyl alcohol and propanal were repeated under

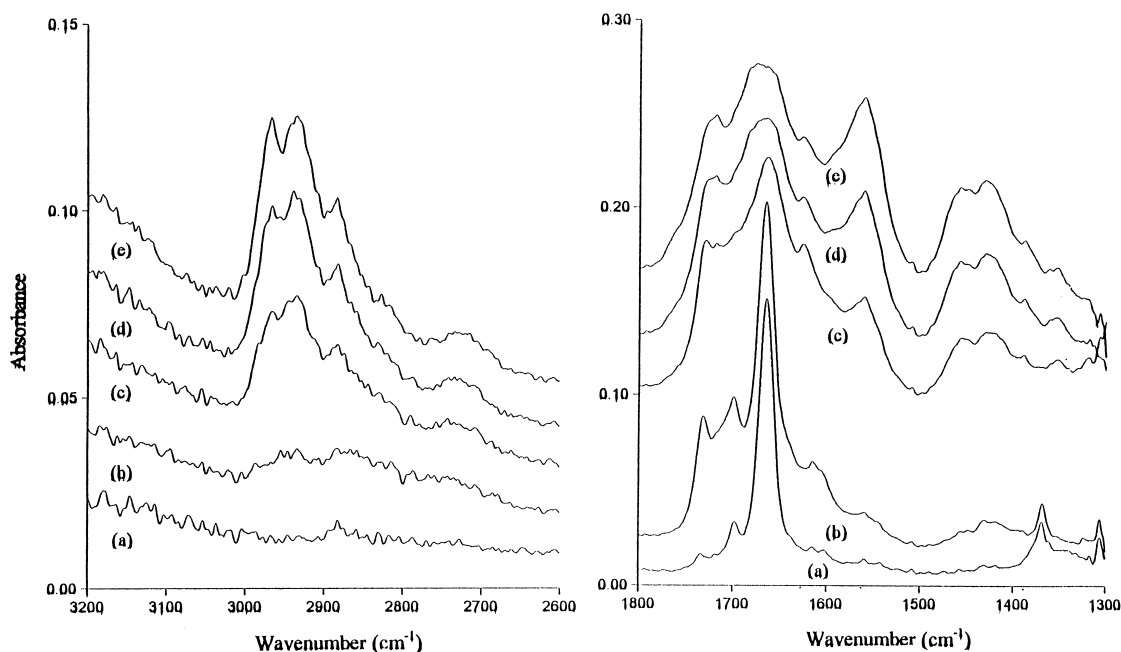


Fig. 6. As for Fig. 5 except reaction involving acrolein for (a) 5 s, (b) 10, (c) 30, (d) 60, (e) 120 min.

exactly the same conditions with alcolein (Fig. 6). The initial spectrum (Fig. 6a) resembled that for acrolein on  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  in the absence of hydrogen, the bands being ascribed to surface  $\sigma$ - and  $\pi$ -complexes of acrolein on cobalt [5]. However, the loss of these complexes and the concomitant formation of adsorbed carboxylate was more rapid when hydrogen was present. The growth of bands at 1559, 1453, 1426 and 1387  $\text{cm}^{-1}$  (Fig. 6e) is more characteristic of propanoate than acrylate [8], a view reinforced by the absence of a band at 1640  $\text{cm}^{-1}$  due to the  $\nu_{\text{C}=\text{C}}$  vibration of surface acrylate [5,6]. The band maximum at 1669  $\text{cm}^{-1}$  due to the O-ligated  $\sigma$ -complex of acrolein, not only weakened in intensity but also broadened and shifted to higher wavenumbers. An increasing component of the broadening maximum at 1679  $\text{cm}^{-1}$  may be ascribed to the corresponding O-ligated  $\sigma$ -complex of propanal on cationic  $\text{Co}^{n+}$  sites [1,5]. The 3100–2800  $\text{cm}^{-1}$  region gave bands which were more characteristic of propanoate than propoxy (Fig. 1) species suggesting that, as for the adsorption of

acrolein alone (Fig. 4), the formation of the latter was partially hindered by  $\text{SO}_2$ -pretreatment. The formation of propanoate on the  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  was much slower than for untreated  $\text{Co}/\text{SiO}_2$  [5]. The spectrum of the gas phase showed that propanal was the dominant reaction product although some unreacted acrolein remained after 2 h reaction at 373 K. For  $\text{Co}/\text{SiO}_2$  which had not been treated with  $\text{SO}_2$ , propanal was an initial product but in the static reaction system conversion to propan-1-ol was complete in 2 h at 373 K [5].

### 3.3. Hydrogenation of acrolein after thiophene pretreatment

Spectra of acrolein alone on thiophene-treated  $\text{Co}/\text{SiO}_2$  initially resembled (Fig. 7a) the spectra of acrolein on  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  (Fig. 4A). However, with increasing time much stronger bands at 1640, 1556, 1443 and 1372  $\text{cm}^{-1}$  due to surface acrylate [5,6] grew for  $\text{Co}/\text{SiO}_2$  pretreated with thiophene rather than

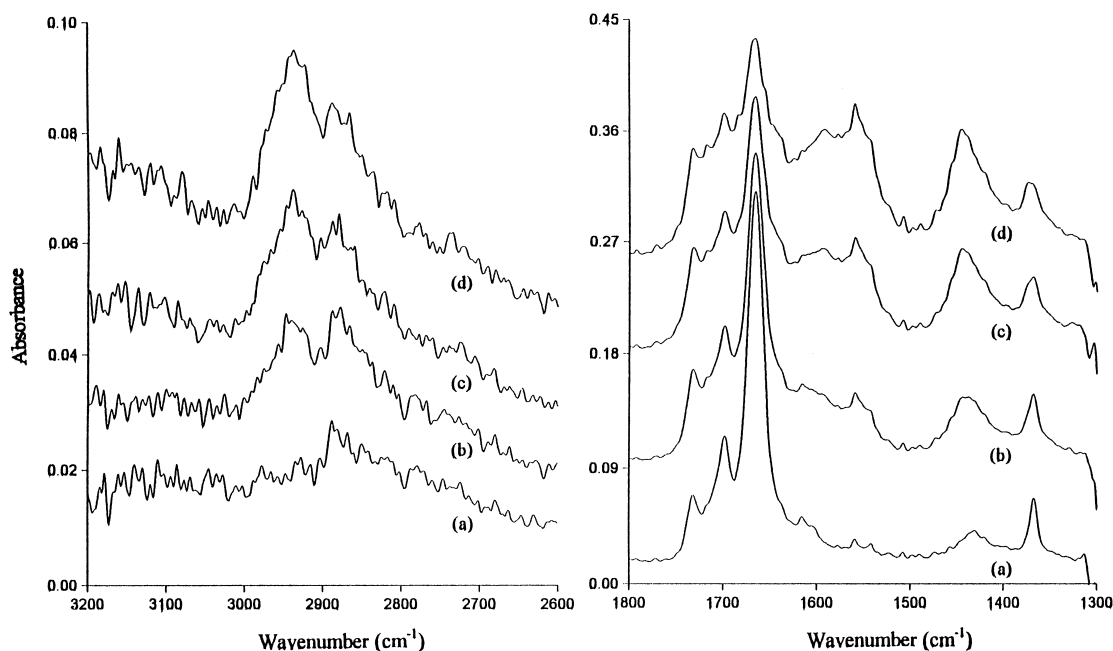


Fig. 7. Spectra of Co/SiO<sub>2</sub> at 373 K after exposure to thiophene (6.7 N m<sup>-2</sup>, 10 min, 373 K), evacuation (1 min, 373 K) and exposure to acrolein (28 N m<sup>-2</sup>, 373 K) for (a) 5 s, (b) 10, (c) 60, (d) 120 min.

SO<sub>2</sub>. the band at 1669 cm<sup>-1</sup> due to the O-ligated  $\sigma$ -complex of acrolein on Co<sup>n+</sup> sites was weakened as surface acrylate appeared. Much less acrylate was formed than for Co/SiO<sub>2</sub> which had not been exposed to thiophene [5]. A band at 1590 cm<sup>-1</sup> (Fig. 7d) for thiophene-treated Co/SiO<sub>2</sub> was present for SO<sub>2</sub>-treated Co/SiO<sub>2</sub> (Fig. 4d) but absent for untreated Co/SiO<sub>2</sub> and may be ascribed to  $\nu_{\text{as}}$  COO<sup>-</sup> vibrations of acrylate species at sites modified by the presence of adsorbed species derived from thiophene or SO<sub>2</sub>. Analysis of the vapour phase after 2 h contact between acrolein and thiophene-treated Co/SiO<sub>2</sub> showed only acrolein to be present, as for untreated Co/SiO<sub>2</sub>.

Repeat of the acrolein adsorption experiment with a higher pretreatment pressure of thiophene (28 N m<sup>-2</sup>) resulted in less acrolein adsorbed via  $\sigma$ -ligation to Co<sup>n+</sup> sites, less acrylate of the type generated on an unmodified Co/SiO<sub>2</sub> surface and more acrylate giving rise to the band at 1590 cm<sup>-1</sup>. After 2 h acrolein was the only component of the vapour phase.

Exposure of Co/SiO<sub>2</sub> to acrolein/hydrogen mixtures at 373 K gave a much weaker band at 1669 cm<sup>-1</sup> due to the  $\sigma$ -complex of acrolein than for acrolein alone (Fig. 8a). Also, the slow growth of bands at 1558, 1468, 1432 and 1382 cm<sup>-1</sup> were consistent with the formation of propanoate rather than acrylate. Hydrogenation of C=C bonds in adsorbed species had occurred. The bands in the  $\nu_{\text{CH}}$  spectral reaction (Fig. 8) were of the form expected (Fig. 1) for the existence of surface propoxy groups on silica with a small contribution from propoxy groups on cobalt. A band growing initially at 1625 cm<sup>-1</sup> (Fig. 8b) resembled a corresponding strong band in spectra of SO<sub>2</sub>-treated Co/SiO<sub>2</sub> exposed to propanal (Fig. 3). The disappearance of the band after 30 min confirmed that C=C bonds were being hydrogenated in the reacting system to give propoxy and propanoate species. The band at 1468 cm<sup>-1</sup> was more intense relative to the band at 1432 cm<sup>-1</sup> than would be expected for its assignment to propanoate alone and the band at 1432 cm<sup>-1</sup> was broader than

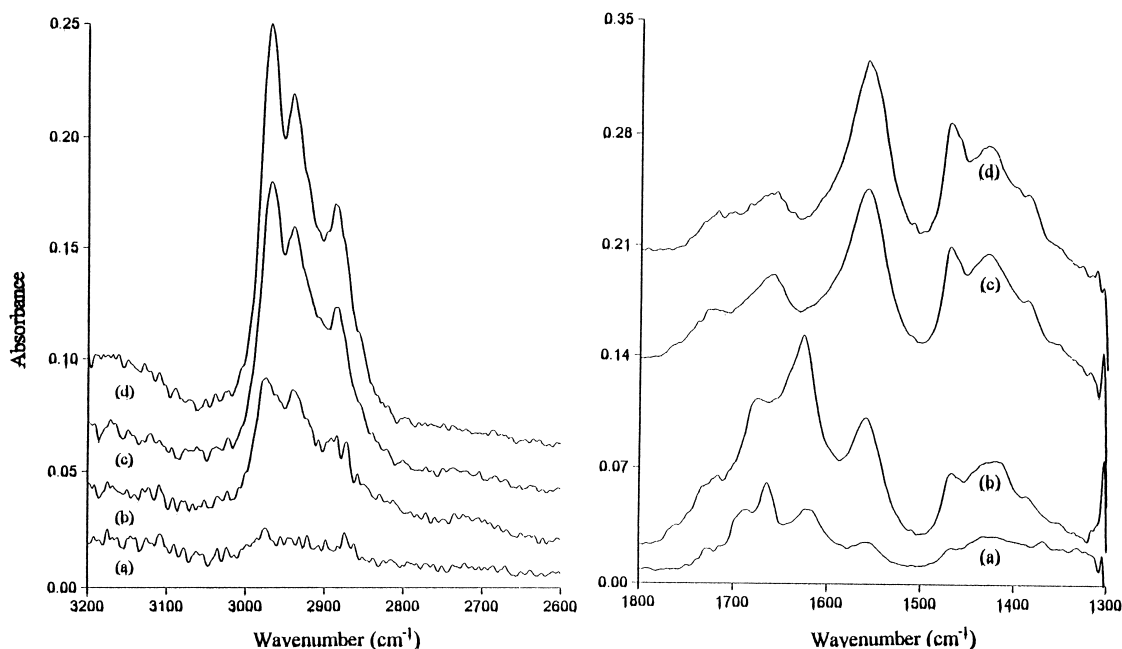


Fig. 8. Reduced Co/SiO<sub>2</sub> exposed to thiophene (28 N m<sup>-2</sup>, 373 K, 10 min), evacuated (1 min, 373 K) and then exposed to an acrolein (28 N m<sup>-2</sup>)/hydrogen (3.3 kN m<sup>-2</sup>) mixture at 373 K for (a) 5 s, (b) 5, (c) 30, (d) 120 min.

expected. These effects were due to contributions from bands at 1462 and 1398 cm<sup>-1</sup> (Fig. 1) due to propoxy groups. Less propanoate and propoxy species were formed on thiophene-treated Co/SiO<sub>2</sub> than on untreated Co/SiO<sub>2</sub> confirming that cobalt sites were poisoned by pretreatment with thiophene at 373 K [1]. Analysis of the vapour phase showed that the conversion of acrolein to propanal (trace after 2 h) and propanol was also slower for Co/SiO<sub>2</sub> which had been pretreated with thiophene. After removal of condensable (at 77 K) gases and cooling to 295 K weak bands due to adsorbed CO appeared at 2014 and 1986 (sh) cm<sup>-1</sup> showing that some decomposition of acrolein or its products of hydrogenation had occurred and also that residual Co<sup>○</sup> sites were available for CO adsorption despite the thiophene modification and generation of adsorbed species from the acrolein/hydrogen mixture. The bands disappeared on evacuation but reappeared on admission of CO to the cell. Similar admission of CO to SO<sub>2</sub>-treated Co/SiO<sub>2</sub> after exposure to acrolein and hydrogen gave, in contrast, a band

at 2050 cm<sup>-1</sup> ascribed to CO on Co<sup>○</sup> sites in low index surface planes [1].

#### 4. Discussion

The present band assignments rely on a detailed study [9] of gas-phase spectra and spectra of adsorbed species on silica and unmodified Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and reduced Co/SiO<sub>2</sub> [5] for all the molecules involved in the acrolein hydrogenation reactions. Reduced Co/SiO<sub>2</sub> contains Co<sup>3+</sup>, Co<sup>2+</sup> and Co<sup>○</sup> sites, all of which were poisoned by SO<sub>2</sub> at 295 K although evacuation at 523 K showed the poisoning was partially reversible at high temperature [1]. Here, SO<sub>2</sub> treatment at 373 K led to partial poisoning of sites responsible for the generation of acrylate or propanoate species from the adsorption of acrolein, propanal, allyl alcohol and propan-1-ol. Surface carboxylate involved reaction between adsorbate molecules and O<sup>2-</sup> ions associated with cationic Co<sup>n+</sup> sites [5]. The poisoning of CO adsorption on Co<sup>n+</sup> sites by SO<sub>2</sub> [1] showed



that the inhibition of carboxylate formation must have involved reaction of  $\text{SO}_2$  with  $\text{O}^{2-}$  ions probably giving sulphite or sulphate species which blocked the subsequent adsorption of aldehydes or alcohols at the same sites.

The formation of acrylate from acrolein or allyl alcohol and propanoate from propanal or propan-1-ol did not lead to acrylic acid or propanoic acid as gaseous products. Carboxylate species on cobalt oxide are difficult to desorb by thermal activation [10] and therefore constituted spectator species in the hydrogenation reactions of acrolein. However, in the presence of hydrogen, surface acrylate derived from acrolein was hydrogenated to give propanoate. The formation of propanoate was slower than for unmodified  $\text{Co}/\text{SiO}_2$  [5] because of  $\text{SO}_2$  poisoning of  $\text{Co}^\circ$  sites [1] which were required for the dissociation of hydrogen.

Alcohol adsorption gave  $\text{SiOAlkyl}$  groups on silica which are also stable to removal at high temperature [11] and did not constitute intermediates in the generation of gaseous products from acrolein/hydrogen mixtures although the results for allyl alcohol hydrogenation showed that  $\text{SiOAllyl}$  groups were transformed into  $\text{SiOPr}$ . Propan-1-ol was not a product of the latter reaction.

Propanal and acrolein were O-ligated to  $\text{Co}^{n+}$  sites to give adsorbed  $\sigma$ -complexes [5]. The existence here of bands due to perturbed carbonyl groups in the  $\sigma$ -complexes confirmed that vacant  $\text{Co}^{n+}$  sites remained after  $\text{SO}_2$  modification of  $\text{Co}/\text{SiO}_2$  at 373 K. Similarly, bands were observed for acrolein due to  $\pi$ -complexes [5] at  $\text{Co}^{n+}$  sites. Additional  $\text{Co}^{n+}$  sites could have been generated by the chemisorption of  $\text{SO}_2$  on  $\text{Co}^\circ$  leading to surface oxide, sulphide and sulphite anions. Acrolein on  $\text{SO}_2$ -modified  $\text{Co}/\text{SiO}_2$  gave a stronger  $\nu_{\text{C=O}}$  infrared band due to  $\sigma$ -complexes than acrolein on unmodified  $\text{Co}/\text{SiO}_2$ . The involvement of  $\sigma$ -complexes in  $\text{C=O}$  hydrogenation may require adjacent  $\text{Co}^\circ$  and  $\text{Co}^{n+}$  sites enabling formation of a di- $\sigma$  complex which, on hydrogenation, gives surface alkoxy groups leading to desorption of

an alcohol [5]. This reaction was completely inhibited by  $\text{SO}_2$  treatment of  $\text{Co}/\text{SiO}_2$  for both acrolein and propanal hydrogenation.

The  $\text{SO}_2$  modification of  $\text{Co}/\text{SiO}_2$  at 373 K completely poisons low coordination  $\text{Co}^\circ$  sites in high index planes but only partially poisons higher coordination sites in low index planes [1]. The mechanism of CHO hydrogenation via a di- $\sigma$  complex at a  $\text{Co}^\circ\text{Co}^{n+}$  site therefore probably occurs on high index planes of incompletely reduced supported cobalt in unmodified  $\text{Co}/\text{SiO}_2$ . The retention of adjacent  $\text{Co}^\circ\text{Co}^\circ$  sites in the catalyst after  $\text{SO}_2$ -treatment is confirmed by the hydrogenation of acrolein to propanal which also proceeds via a di- $\sigma$  complex [12]. This reaction may occur on low index planes which also, after  $\text{SO}_2$  modification, provide residual  $\text{Co}^\circ$  sites for hydrogen dissociation. The rate of formation of propanal from acrolein was less for  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  than for  $\text{Co}/\text{SiO}_2$  showing in accordance with CO adsorption data [1], that low index planes were partially poisoned by  $\text{SO}_2$ . Treatment of  $\text{Co}/\text{SiO}_2$  with  $\text{SO}_2$  followed by evacuation at 373 K and admission of CO gave an infrared band at  $2067\text{ cm}^{-1}$  due to CO on  $\text{Co}^\circ$  in low index planes [1].

Propan-1-ol on silica-supported metals leads not only to  $\text{SiOPr}$  groups on silica but also propoxy groups on the metal surfaces [13]. Comparison of the intensities of bands due to propoxy groups on silica, unmodified  $\text{Co}/\text{SiO}_2$  and  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  showed an order of intensities according to catalyst of  $\text{Co}/\text{SiO}_2 > \text{SO}_2\text{-Co}/\text{SiO}_2 > \text{SiO}_2$ . The formation of propoxy groups on cobalt was therefore only partially poisoned by  $\text{SO}_2$  modification at 373 K. However, a contrasting result for modified and unmodified  $\text{Co}/\text{SiO}_2$  was the complete absence of propan-1-ol as a product from acrolein, propanal and allyl alcohol hydrogenation over  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  whereas untreated  $\text{Co}/\text{SiO}_2$  gave propan-1-ol as the dominant product from all three hydrogenation reactions.

Despite reports of high selectivities to unsaturated alcohols in  $\alpha,\beta$ -unsaturated aldehyde

hydrogenation over cobalt catalysts [14–17] and that  $\text{SO}_2$  can promote selectivity to unsaturated alcohols over copper catalysts [2,3], the present analyses gave no evidence of allyl alcohol as a product of acrolein hydrogenation. This result cannot be directly attributed to  $\text{SO}_2$ -treatment because unmodified  $\text{Co}/\text{SiO}_2$  also gave no allyl alcohol [5]. A marked contrast in results was that  $\text{Co}/\text{SiO}_2$  caused 100% hydrogenation of allyl alcohol to propan-1-ol but the reaction was completely poisoned by  $\text{SO}_2$  modification. Thus, the absence of allyl alcohol from acrolein for the  $\text{SO}_2$ -treated catalyst was not due its own transitory appearance as an intermediate which was rapidly converted to another product. Propanal was a reaction product from acrolein but negligible propanal resulted from allyl alcohol isomerisation. The complete poisoning of  $\text{C}=\text{C}$  hydrogenation for allyl alcohol was not matched for acrolein where  $\text{C}=\text{C}$  hydrogenation to propanal readily took place. The ease of  $\text{C}=\text{C}$  hydrogenation apparently depended on the oxygen containing group (OH or CHO) in the reacting molecule. Sulphur dioxide induced the different behaviour for allyl alcohol and acrolein. A tentative suggestion would be that  $\text{C}=\text{C}$  hydrogenation over  $\text{SO}_2$ -modified  $\text{Co}/\text{SiO}_2$  requires the availability of  $\text{Co}^\circ\text{Co}^\circ$  sites in low index surface planes for the formation of a di- $\sigma$  complex by adsorption at the alkenyl bond. Weak  $\sigma$  ligation via CHO groups to  $\text{Co}^\circ$  sites may hinder but does not inhibit formation of the di- $\sigma$  complex and therefore acrolein hydrogenation to propanal proceeds satisfactorily, albeit at a reduced rate compared with  $\text{Co}/\text{SiO}_2$  for which  $\text{SO}_2$  pretreatment had not partially poisoned low index planes. The products of the partial poisoning at 373 K will generate surface species ( $\text{O}^{2-}$ , sulphito groups) with basic character thus promoting proton transfer from incoming alcohol molecules. The dissociative adsorption of allyl alcohol therefore results in strongly adsorbed alkoxy groups at  $\text{Co}^\circ$  sites which become poisoned as active sites for  $\text{C}=\text{C}$  hydrogenation. An additional explanation might be that the reaction of alcohols with silanol

groups giving  $\text{SiOAlkyl}$  groups also leads to water which poisons  $\text{C}=\text{C}$  hydrogenation via a di- $\sigma$ -complex over residual  $\text{Co}^\circ$  sites on low index surface planes. The favourability of this after  $\text{SO}_2$ -treatment could be linked to the presence of adsorption products from  $\text{SO}_2$  which favour water dissociation at the surface.

The foregoing explanation of the different hydrogenation behaviour of acrolein and allyl alcohol assumes that  $\text{Co}^\circ\text{Co}^\circ$  sites on low index planes remain available after  $\text{SO}_2$  treatment to enable di- $\sigma$  addition complexes to form at the alkenyl segment of acrolein molecules. However, CO adsorption shows that a high proportion of  $\text{Co}^\circ$  sites are poisoned by  $\text{SO}_2$ . If this results in the absence of adjacent  $\text{Co}^\circ$  sites required by the di- $\sigma$  complex then an alternative explanation for the hydrogenation behaviour must be found. One possibility would be that the  $\sigma$ -complexed acrolein O-ligated to  $\text{Co}^{n+}$  sites can be hydrogenated to give  $\sigma$ -complexed propanal which desorbs as a reaction product. The  $\text{Co}^\circ$  sites, which CO adsorption shows are present on low index planes, would be responsible for the dissociation of hydrogen. The mechanism would be analogous to the observed hydrogenation of irreversibly adsorbed  $\text{SiOAllyl}$  and acrylate anions on the  $\text{SO}_2$ -treated surface. Allyl alcohol will be strongly chemisorbed at  $\text{Co}^{n+}$  sites to give alkoxy groups, which may be hydrogenated to propoxy groups, but these remain strongly adsorbed and do not lead to propan-1-ol in the gas phase.

The hydrogenation of acrylate to propanoate on  $\text{Co}^{n+}$  and  $\text{SiOAllyl}$  to  $\text{SiOPr}$  on silica in  $\text{Co}/\text{SiO}_2$  suggests that alkoxy groups on cobalt may also be hydrogenated to propoxy groups. However, strong adsorption of propoxy groups on the  $\text{SO}_2$ -modified low index planes precluded their desorption as propan-1-ol. The dominant reactions of alcohols with  $\text{SO}_2$ -treated  $\text{Co}/\text{SiO}_2$  in the absence of hydrogen involved oxidation to give traces of acrolein from allyl alcohol and propanal from propan-1-ol. The adsorbed products of oxidation were acrylate and propanoate. However, both aldehyde and car-

boxylate formation were much less for the SO<sub>2</sub>-treated catalyst than for unmodified Co/SiO<sub>2</sub> showing that the reactive surface species were oxide anions associated with Co<sup>n+</sup> ions on the surface of incompletely reduced cobalt [1].

The formation of 2-methylpenten-2-al from propanal over Co/SiO<sub>2</sub> catalysts [5,7] involves an aldol condensation reaction. The mechanism of the similar reaction of propanone giving mesityl oxide over rutile was shown to involve ligated propanone on Ti<sup>4+</sup> sites giving adsorbed enolate via proton transfer to basic O<sup>2-</sup> or OH<sup>-</sup> ions followed by addition of a further propanone molecule with elimination of OH<sup>-</sup> to the surface [18]. Mesityl oxide remained O-ligated to Ti<sup>4+</sup> sites. The formation of gaseous 2-methylpenten-2-al here was related to a band at 1625 cm<sup>-1</sup> due to the  $\nu_{C=C}$  stretching vibrations of the adsorbed product. The amounts of the gaseous and adsorbed products were in the sequence SO<sub>2</sub>/propanal > SO<sub>2</sub>/propanal/H<sub>2</sub> > propanal > propanal/H<sub>2</sub>. Modification with SO<sub>2</sub> enhanced the aldol condensation reaction whereas hydrogen had an inhibiting effect with or without SO<sub>2</sub> pretreatment. Sulphur dioxide, as shown by the results for acrolein adsorption, generated additional sites for the adsorption of C=O compounds via  $\sigma$ -ligation to Co<sup>n+</sup> ions. Furthermore, dissociative adsorption of SO<sub>2</sub> formed oxidic species which were sufficiently basic to promote proton transfer from propanal, thus giving adsorbed enolate as a precursor of adsorbed 2-methylpenten-2-al which desorbed to give the gaseous product. This reaction does not depend on the availability of Co<sup>0</sup> sites but relies on the availability of Lewis acidic Co<sup>n+</sup> sites and Brønsted basic O<sup>2-</sup> ions, i.e., the oxidic characteristics of the modified surface. Inhibition of the reaction by hydrogen, which was complete for unmodified Co/SiO<sub>2</sub> [5], involved dissociation of H<sub>2</sub> on Co<sup>0</sup> sites and hydrogenation of C=C bonds in adsorbed enolate leading to propoxy species and hence propan-1-ol as the gaseous product.

In general, the behaviour of the acrolein hy-

drogenation reaction over thiophene-modified Co/SiO<sub>2</sub> gave intermediate results between those for the SO<sub>2</sub>-treated and unmodified catalysts. Thiophene is chemisorbed on cobalt at 373 K leaving sulphide on the metal surface [19]. Thiophene was a strong poison of CO adsorption on the present catalysts [1]. The generation of acrylate, and hence propanoate by hydrogenation, occurred to a lesser extent on Co/SiO<sub>2</sub> after exposure to thiophene at 373 K. The ability of acrolein to  $\sigma$ -bond to Co<sup>n+</sup> sites was also reduced by sulphiding. The availability of Co<sup>n+</sup> was partially blocked by sulphiding although the infrared band at 1590 cm<sup>-1</sup>, not observed for unmodified Co/SiO<sub>2</sub> [5], also suggested that a further configuration of adsorbed carboxylate was induced by adsorbed sulphide. This may be specifically associated with Co<sup>2+</sup> sites since Co<sup>3+</sup> are more readily completely poisoned by thiophene [1]. Attribution of a band at 1590 cm<sup>-1</sup> to  $\nu_{C=C}$  vibrations of acrolein coordinated to metal cations in cobalt molybdate [20] seems less likely to be valid here in view of the absence of the band for unmodified Co/SiO<sub>2</sub> and the general site-blocking effect of sulphide on adsorptive interactions.

Acrolein hydrogenation over Co/SiO<sub>2</sub> after thiophene treatment gave slower conversion to propanal than unmodified Co/SiO<sub>2</sub> but unlike SO<sub>2</sub>-treated catalyst, also allowed C=O hydrogenation leading to propan-1-ol. Partial decomposition of acrolein with hydrogen to CO on low coordination Co<sup>0</sup> sites shows the availability of these sites during acrolein hydrogenation over thiophene-modified Co/SiO<sub>2</sub> supporting the argument that C=O hydrogenation requires low coordination sites for catalytic activity. These sites were poisoned by SO<sub>2</sub> and propanol was then not a detectable reaction product.

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