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FTIR study of CO adsorption on Pd / SiO_2 and Pd–Cu / SiO_2 treated with sulphur dioxide

Sheikha S. Ashour, Jillian E. Bailie, Colin H. Rochester * and James Thomson
Chemistry Department, Dundee University, Dundee DD1 4HN, UK

Graham J. Hutchings
Leverhulme Centre for Innovative Catalysis, Chemistry Department, Liverpool University, PO Box 147,
Liverpool L69 3BX, UK

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Infrared spectra are reported of Pd / SiO_2 and Pd–Cu / SiO_2 exposed at 295 K to either CO followed by SO_2 or SO_2 followed by CO. Chemisorptive interaction of SO_2 with bridging CO sites on Pd {100} faces created cationic Pd sites which adsorbed CO linearly. Multibonding CO sites on Pd {111} faces and linear CO sites were poisoned by weak non-dissociative SO_2 adsorption, and could be regenerated by evacuation. Pd / SiO_2 was more resistant than Cu / SiO_2 to SO_2 poisoning but for Pd–Cu / SiO_2 the poisoning of Pd was promoted by the presence of Cu.

Keywords: Pd–Cu catalysts, SO_2 adsorption, sulphur poisoning

1. Introduction

Sulphur dioxide acts as a poison of supported metal catalysts but in controlled doses can lead to significant changes in reaction selectivity with the retention of some catalyst activity [1]. The effects of sulphur dioxide on Cu / SiO_2 and Cu / Al_2O_3 catalysts have been probed by IR study of CO adsorption [2,3] and related to resulting changes in selectivity in the hydrogenation reaction of crotonaldehyde [1]. Similar studies involving thiophene as modifier [1–4] have been extended to Pd / SiO_2 and Pd–Cu / SiO_2 catalysts [5]. In the mixed metal catalysts Pd sites were more resistant than Cu sites to interaction with thiophene. Partially modified surfaces therefore favoured C=C hydrogenation in accordance with the behaviour of unmodified Pd / SiO_2 rather than C=O hydrogenation, more favourable over Cu, which was poisoned by low doses of thiophene. This IR study of CO adsorption on Pd / SiO_2 and Pd–Cu / SiO_2 with and without co-adsorption of sulphur dioxide was aimed at assessing the influence of sulphur dioxide on adsorption sites in the mixed metal catalysts. Sulphur dioxide is at least in part dissociatively adsorbed on Pd [6] and, depending on temperature, may give chemisorbed SO, S, O and SO_4 species [7]. Despite reports to the contrary [8,9] there is also evidence for the chemisorption of sulphur dioxide at ca. 300 K on Cu(100) [10] and oxide-supported Cu [2,3].

2. Experimental

Catalysts were prepared from silica (Cab-O-Sil M5, 200 $m^2\ g^{-1}$) and copper(II) acetate monohydrate and palladium(II) acetate as before [5]. The final stage involved reduction in hydrogen (60 $cm^3\ min^{-1}$) at 523 K (16 h) before evacuation (523 K, $\frac{1}{2}$ h) and cooling to ca. 295 K for spectroscopic examination. Reduced Pd / SiO_2 contained 8.3 wt% Pd which is equivalent to 8.51×10^{-4} mol of Pd per gram of silica. The mixed metal catalyst also contained 8.51×10^{-4} mol of metal per gram of silica made up of equimolar amounts of Pd and Cu. Spectra were recorded of pressed discs of catalyst by transmission spectroscopy at 4 cm^{-1} resolution.

3. Results

Spectra of CO on Pd / SiO_2 (figure 1 (a)) contained bands at 2095, 1995 and 1950 cm^{-1} due to linearly adsorbed CO [11–13], bridge-bonded CO on {100} faces of Pd [14], and multibonded CO on {111} faces of Pd [15,16], respectively. Subsequent addition of SO_2 at pressures in the range 27–1995 N m^{-2} with CO (267 N m^{-2}) retained in the cell had only small effects on the spectra (figure 1 (b)) compared with the large changes which occurred for Cu / SiO_2 with only 13 N m^{-2} of SO_2 added [2]. The bands due to bridged and multibonded CO on Pd were unaffected by SO_2, but linearly bonded CO was increasingly displaced with increasing SO_2 pressure. The band at 2095 cm^{-1} was 50% reduced in intensity for an

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* To whom correspondence should be addressed.

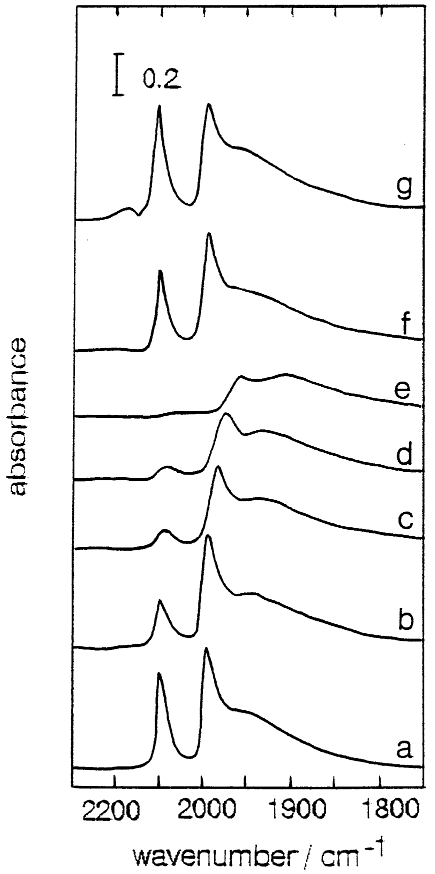

Figure 1. Spectra of Pd/SiO$_2$ exposed to (a) CO (267 N m^{-2}), and (b) CO (267 N m^{-2}) + SO$_2$ (1995 N m^{-2}), followed by evacuation for (c) 1, (d) 5 and (e) 30 min before re-admission of CO at (f) 267 and (g) 3990 N m^{-2}.

SO$_2$ pressure of 1995 N m^{-2}. Subsequent evacuation at ca. 295 K caused reductions in the intensities of all three bands due to adsorbed CO and shifts to 2066, 1959 and 1904 cm^{-1} (figure 1 (c)–(e)), which may be attributed to decreasing dipolar coupling effects [17] with decreasing surface coverage. Re-admission of CO restored the bands to their positions and intensities before admission of SO$_2$. Evacuation apparently desorbed SO$_2$ which impeded linearly adsorbed CO.

A band at 1343 cm^{-1} superimposed on bands due to SO$_2$ gas was due to SO$_2$ molecules which were weakly adsorbed primarily via hydrogen bonding interactions with silanol groups on the silica support. The band due to vibrations of silanol groups was perturbed to 3657 cm^{-1} in the presence of SO$_2$.

Slow changes in spectra of CO on Cu/SiO$_2$ following admission of sulphur dioxide have previously been reported [2]. Slow spectral changes were also observed here during similar experiments. However, these effects for Cu/SiO$_2$, Pd/SiO$_2$ and Pd–Cu/SiO$_2$ have now been shown to be due to slow rates of diffusion of SO$_2$ gas to the catalyst surfaces in a vacuum line already containing CO.

The results for Pd/SiO$_2$ which had been exposed to SO$_2$ before CO adsorption (figure 2) were in marked contrast to those for SO$_2$ addition to a CO-covered surface. Even a small pressure of SO$_2$ caused the complete disappearance of the band at 1995 cm^{-1} due to bridged CO and an appreciable enhancement in the band at ca. 2100 cm^{-1} due to linearly bonded CO. Adsorption of SO$_2$ on {100} faces of Pd impedes the formation of bridged CO by decreasing the surface population of adjacent Pd atoms available for bridging, but increases the population of isolated Pd atoms receptive for linearly adsorbed CO. The band due to multibonded CO was of similar intensity with (figure 1 (a)) and without (figure 2 (a)) treatment with SO$_2$ at low pressure suggesting that the {111} planes of Pd were less sensitive than the {100} planes to SO$_2$ adsorption. A narrow band at 1968 cm^{-1} on the high wavenumber side of the broad band envelope due to multibonded CO can be ascribed to CO on residual bridging sites which were too far apart for dipolar coupling effects to operate.

Increasing doses of SO$_2$ (figure 2 (b)–(d)) poisoned both linear and multibonding sites although the latter not completely as a broad band at 1892 cm^{-1} appeared when CO was added to the poisoned surface. Subsequent

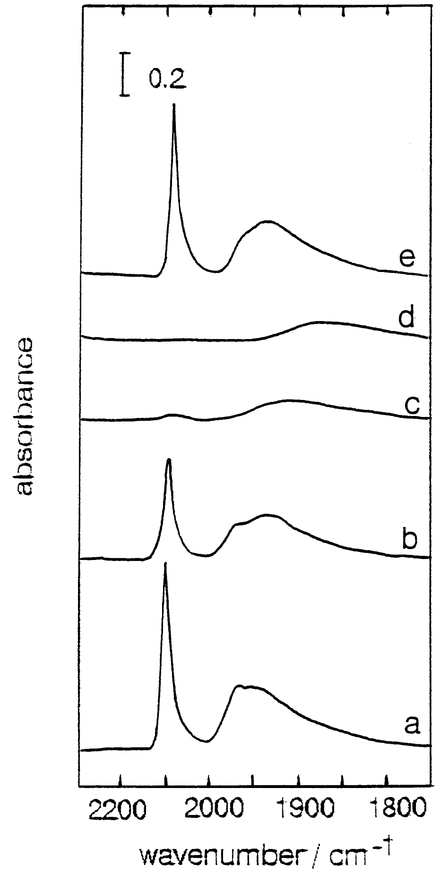

Figure 2. Spectra of Pd/SiO$_2$ exposed to CO (267 N m^{-2}) after prior admission of SO$_2$ at (a) 27, (b) 80 and (c) 1995 N m^{-2}, followed by (d) evacuation for 30 min, and (e) re-admission of CO (267 N m^{-2}).

evacuation at 295 K followed by re-admission of CO showed that the effects of SO_2 on sites which adsorbed CO in the linear or multibonded form were reversible, but that bridging sites remained poisoned. The resulting spectrum (figure 2 (e)) resembled that for the partially poisoned catalyst (figure 2 (a)).

The spectrum of CO adsorbed on Pd–Cu/SiO_2 (figure 3 (a)) contained bands at 2125, 2100 (sh), 2064, 1962 and 1950 (sh) cm^{-1}. In accordance with corresponding assignments of bands in spectra of CO on Pd–Cu/Al_2O_3 [13], these have been ascribed [5] to CO on cationic Cu sites, linear CO on Cu^0, linear CO on Pd, bridged CO on Pd, and multibonded CO on Pd, respectively. A more detailed discussion of the band assignments based on the variations in band positions with changing Cu/Pd ratios [5] and on existing literature is given elsewhere [5]. Changes induced by the addition of SO_2 were reminiscent of the separate effects of SO_2 on CO adsorbed on Cu/SiO_2 [2] and Pd/SiO_2. The band due to CO on Cu^0 was diminished in intensity in parallel to the growth of the maximum at 2125 cm^{-1} (figure 3 (b) and (c)). The adsorption of SO_2 on Cu sites promoted electron transfer from Cu to surface products but did not block the interaction between CO and the resulting Cu atoms with cationic character. Treatment of Cu alone on SiO_2 with SO_2 similarly gave a diminution in a band due to CO on Cu^0 and the appearance of a band at 2121 cm^{-1} due to CO on cationic sites [2]. The conversion of Cu^0 to Cu^+ sites which resulted from SO_2 adsorption did not lead to any new types of Cu^0 site which were not present in the absence of SO_2. Oxidation of Cu^0 to Cu^+ by reaction with N_2O also failed to cause reconstruction effects involving Cu^0 sites [18].

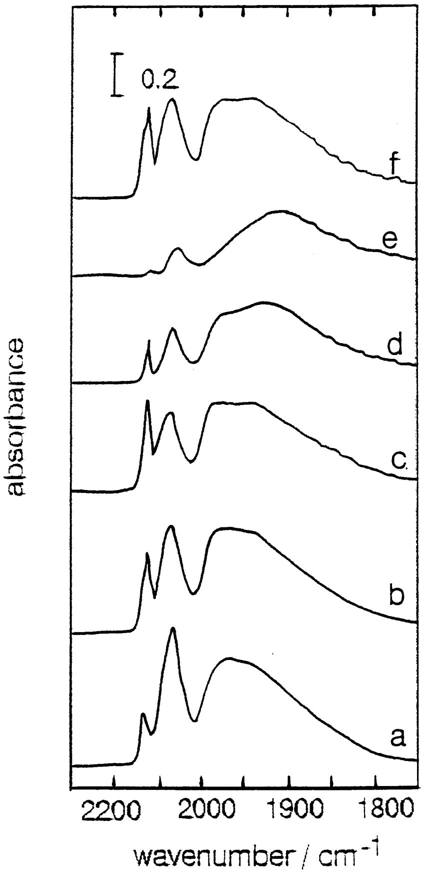

Figure 3. Spectra of Pd–Cu/SiO_2 exposed to (a) CO (267 N m^{-2}), (b) CO + SO_2 (80 N m^{-2}) and (c) CO + SO_2 (1330 N m^{-2}), followed by evacuation for (d) 5 and (e) 45 min, and (f) re-admission of CO (267 N m^{-2}).

The band due to linear CO on Pd was reduced in intensity but bridged and multibonded CO molecules were only comparatively slightly affected by exposure to SO_2. Thus, Pd was apparently more resistant than Cu to surface modification by adsorbed SO_2. Furthermore, the Pd component of the mixed metal surface was restored to its unmodified state by evacuation (figure 3 (d) and (e)) as subsequent admission of CO (figure 3 (f)) gave the initial bands due to CO on Pd (figure 3 (a)) back again. In contrast, the copper component remained modified, the spectrum retaining the band at 2125 cm^{-1} characteristic of cationic sites partially derived from electron transfer from Cu to Pd [19] but additionally derived from electron transfer from Cu to the surface products of chemisorption of SO_2. Leung et al. [10] concluded that SO_2 was chemisorbed on Cu^0 at 295 K.

The admission of SO_2 before CO to Pd–Cu/SiO_2 produced results similar to those for Cu/SiO_2 in the absence of Pd. Increasing pressures of SO_2 intensified the band at 2125 cm^{-1} due to CO on cationic sites (figure 4 (a)–(c)). Evacuation weakened the band (figure 4 (e)) which, however, was restored on re-admission of CO (figure 4 (f)). By comparison, the adsorption of CO on the Pd component (figure 3 (a)) was strongly poisoned by SO_2 pretreatment (figure 4 (a)) even at low SO_2 pressures. Compared to Pd/SiO_2 the addition of the Cu component appeared to promote the poisoning of Pd sites by SO_2. Furthermore, evacuation followed by re-admission of CO failed to generate the strong band at ca. 2100 cm^{-1} (figure 4 (f)) observed for Pd/SiO_2 (figure 2 (e)). The complete poisoning by SO_2 of Pd sites for the linear adsorption of CO could be reversed by evacuation at 295 K for Pd/SiO_2 but not for Pd–Cu/SiO_2.

4. Discussion

Bands due to CO on Pd/SiO_2 are ascribed to adsorption on {100} and {111} exposed faces [14–16] or at edge or corner sites in small Pd particles. The existence of {100} and {111} planes is more favourable than {110} planes on small particles [20] and therefore reconstruction effects involving {110} planes [21] are unlikely to be significant in the present context. Band shifts associated with dipolar coupling effects resulting from dilution of Pd with Cu are discussed in detail elsewhere [5].

The ease of desorption of CO from polycrystalline

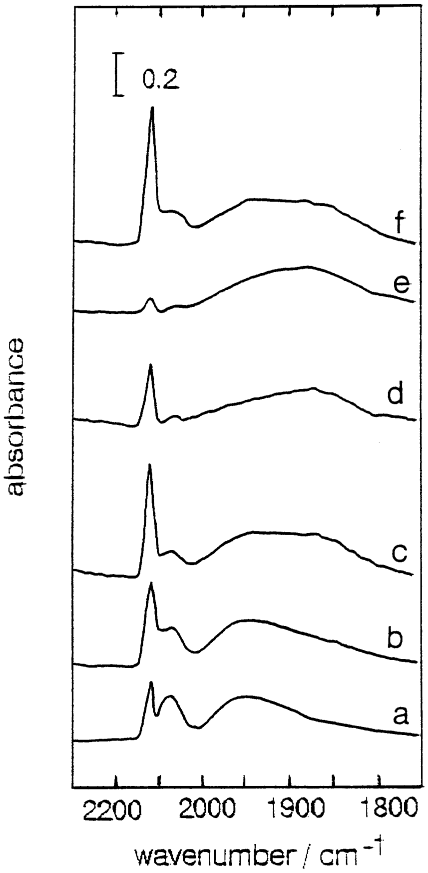

Figure 4. Spectra of Pd–Cu/SiO_2 exposed to CO (267 N m^{-2}) after admission of SO_2 at (a) 27, (b) 80, (c) 800 and (d) 1995 N m^{-2}, followed by (e) evacuation (30 min), and (f) re-admission of CO (167 N m^{-2}).

Pd is in the sequence linear > bridged > multibonded [5,11] and this is reflected in the resistance of bridged and multibonded CO to displacement by SO_2. The hindering of SO_2 adsorption by bridged CO on {100} faces of Pd [4] contrasts with the chemisorption of SO_2 on clean {100} faces (figure 2) suggesting that a weakly adsorbed form of SO_2 constitutes a precursor of chemisorbed SO_2 and cannot gain access to bridging sites covered by pre-adsorbed CO. Pre-adsorbed sulphur also blocks SO_2 decomposition on Pd(100) [7].

The adsorption of multibonded CO on {111} faces [15,16] was much less influenced by SO_2 pretreatment than was the adsorption of bridging CO on {100} planes. Vázquez et al. [22] similarly reported that sulphiding of Pd in Pd/SiO_2 by H_2S occurred more rapidly on some exposed planes than others, and the unsulphided Pd persisted in some small particles. Chemisorption of SO_2 has been observed on evaporated films of Pd [6] and Pd(100) [7] at lower temperatures than 295 K. Chemisorption here blocked bridged sites for CO adsorption but initially generated additional sites for the linear adsorption of CO. The shift of the band at 2059 cm^{-1} (figure 1) due to linear Pd^0–CO to ca. 2100 cm^{-1} (figure 2) after treatment with SO_2 resembles a similar effect of oxidation of Pd/SiO_2 on CO adsorption [11]. This further supports the contention, in accordance with the results of Burke and Madix for Pd(100) [7], that SO_2 was chemisorbed on {100} faces of Pd particles with the generation of surface O and SO species. This result is also added confirmation of the assignment [14] of the band at 1995 cm^{-1} to bridged CO specifically on exposed {100} faces of Pd.

The position of the band at 2100 cm^{-1} for linear CO on SO_2-treated Pd/SiO_2 suggests that the adsorbing Pd atom sites were electron deficient with respect to Pd^0 which gave the band at 2095 cm^{-1}. Chemisorption of SO_2 gave O and SO species which promoted electron transfer from vicinal Pd atoms thus creating cationic Pd sites for CO adsorption. The enhancement of linear sites at the expense of bridged sites also accompanies oxidation of Pd/SiO_2 with O_2 [11]. Pd becomes electron deficient in the presence of adsorbed sulphur [23] as well as oxygen. Cationic Pd is more resistant to sulphur than Pd^0 [24]. Initial poisoning of bridged sites on {100} planes by SO_2 creates isolated cationic sites (figure 2 (a)) which only become themselves poisoned after exposure to much higher pressures of SO_2 (figure 2 (c)). The poisoning of isolated sites and multibonding sites on Pd {111} planes [15,16] probably involved weak non-dissociative adsorption of SO_2 as the effects of poisoning were removed by evacuation at 295 K.

Pd in Pd/SiO_2 exposed to CO was more resistant than Cu in Cu/SiO_2 [2] or Cu/Al_2O_3 [3] exposed to CO towards interaction with SO_2. Previous reports have concluded that Pd has a higher tolerance of sulphur than has Cu [22,23]. SO_2 is chemisorbed on Cu [2,3,10] and on Pd(100) [7]. Here, for Pd–Cu/SiO_2 exposed to CO, the Cu component interacted more readily than Pd with SO_2. However, in the absence of pre-adsorbed CO the Pd component became more susceptible to poisoning than Pd in Pd/SiO_2. Infrared spectra of Pd–Cu/SiO_2 with various metal compositions exposed to CO [5] support the conclusion [14,27–29] that Pd–Cu mixtures give homogeneous bimetallic alloys. The spectra of adsorbed CO show that exposed Pd and Cu atoms mutually influenced each other and therefore probably existed in common surface planes. The high propensity of Cu to promote dissociative adsorption of SO_2 was accompanied by an enhancement in the reactivity of surface Pd towards SO_2. In particular, Pd sites for the linear adsorption of CO and for CO multibonding in {111} planes were much more reactive towards SO_2 in the presence rather than in the absence of Cu. Bridged sites on Pd {100} faces were less prominent for Pd–Cu/SiO_2 than for Pd/SiO_2 because of the diluent geometric effect of Cu [5]. However, the spectra reveal that the bridged sites were also at least as reactive towards SO_2 in Pd–Cu/SiO_2 as in Pd/SiO_2. One explanation would be that the products of dissociative adsorption of SO_2 on Cu migrate to Pd sites where they poison the subsequent adsorption of CO. Alternatively, an electronic effect may be invoked in which electron transfer from Cu to Pd occurs [19] giving electron-rich Pd atoms which may be more prone to sulphur poisoning [24]. The band at 2125 cm^{-1} (figure 3 (a)) due to CO on cationic sites [17] provides evidence [5] for electron transfer from Cu.

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