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CO oxidation over alumina supported platinum catalyst

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The oxidation of CO over Pt/Al_2O_3 has been studied using combined FTIR and *in situ* reaction cell. During reaction the stretching frequency of the adsorbed carbonyl species remained constant over a temperature range during which a change in the CO conversion occurred. The range of conversion during which this invariance was observed was considerably greater for used catalyst than for fresh Pt/Al_2O_3. The formation of islands of CO and the role of these in the overall reaction mechanism is discussed.

Keywords: CO oxidation; Pt; FTIR; CO islands

1. Introduction

Platinum is currently a component in the three-way catalyst for the control of automobile exhaust emissions, where its main role is in the oxidation of CO and hydrocarbons [1]. As a result of this practical importance and due to the apparent simplicity of this reaction for studies at a fundamental level, the oxidation of CO over Pt has received considerable attention [2,3]. It is most likely that the reaction proceeds via a Langmuir-Hinshelwood mechanism and that under certain conditions the adsorbed reactants may exist on the surface in distinct regions [2]. Since high local coverage of CO may exist during reaction, infrared spectroscopy may be used in such studies since this phenomenon is displayed in the form of invariance in the carbonyl stretching frequency [4–6]. The present paper outlines the relationship between the extent of reaction and the presence of CO islands and also outlines the structure-sensitive nature leading to the formation of these islands.

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2. Experimental

1% platinum catalyst was prepared by aqueous impregnation of Degussa-C γ-Al_2O_3 by H_2PtCl_6 followed by air drying at 373 K. Self-supporting discs of the dried material (100 mg, 25 mm diameter) were heated in a flow of oxygen at 673 K for 1 h and transferred to a stainless steel infrared cell [7]. Samples were then reduced in a flow of H_2/Ar for 2 h at 573 K in accordance with previous studies [7,8] and then cooled in dynamic vacuum. The catalyst was then exposed to a flow (50 cm^3 min^{-1}) of CO(1%)/O_2(16%) in nitrogen at 293 K and then heated in a linear temperature ramp (10 K min^{-1}) to 573 K. Spectra (4 cm^{-1}, 4 scan average) were recorded using a Perkin Elmer 1710 FTIR spectrometer coupled to a 7500 computer.

3. Results

Fig. 1 shows the rate of CO_2 formation as a function of temperature as monitored by the absorbance at 2361 cm^{-1} due to the R-branch of gaseous CO_2. For the catalyst after initial reduction, the rate gradually increased above 373 K reaching a maximum level at 458 K. On reaching 573 K, the supply of O_2 was stopped and adsorbed oxygen removed in the CO/N_2 flow. The catalyst was

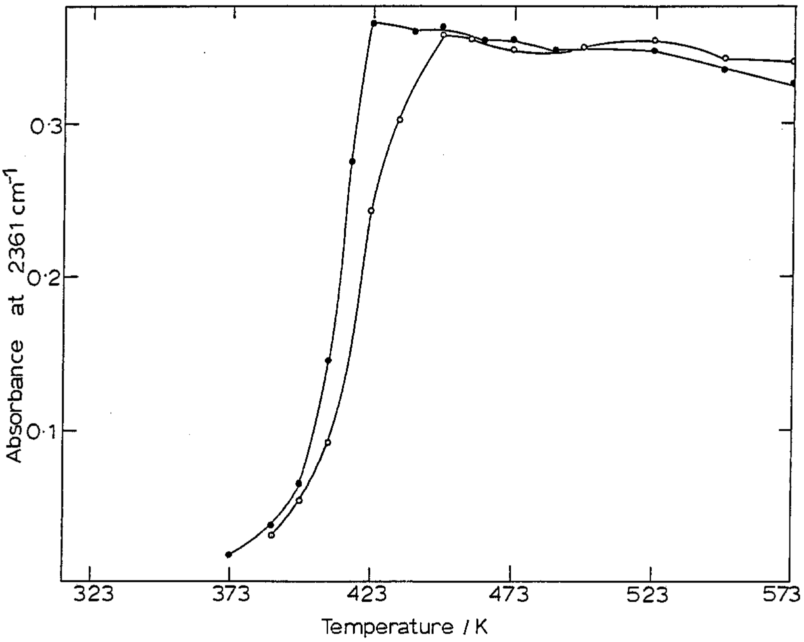

Fig. 1. Band intensity at 2361 cm^{-1} due to CO_2 gas formed in a flow of CO/O_2 against catalyst temperature for Pt/Al_2O_3 after primary reduction ○ and re-reduction ●.

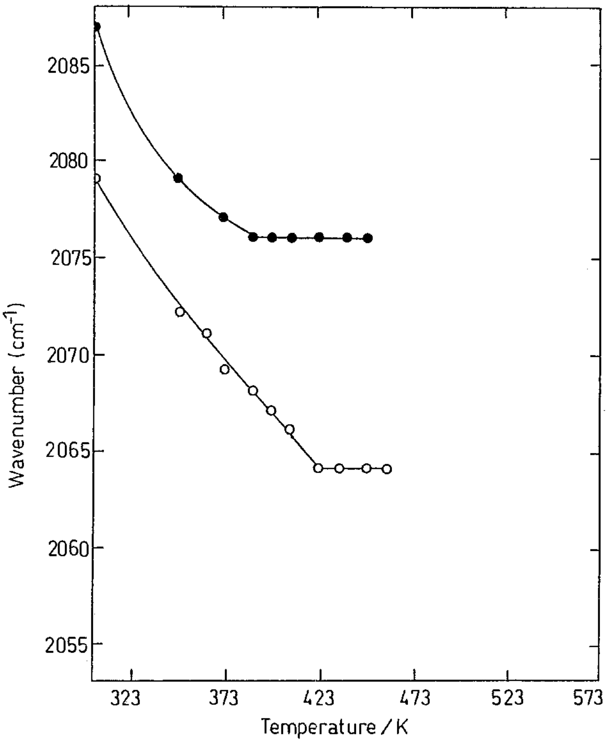

Fig. 2. Band position of linearly adsorbed carbonyl species as a function of catalyst temperature for Pt/Al_2O_3 after primary reduction ○ and re-reduction ●.

then cooled to 300 K in N_2 and then reduced in H_2/Ar according to the standard procedure. The catalyst was then heated in an equivalent reaction mixture under identical temperature program conditions. At low CO conversion the fresh and re-reduced catalyst exhibited a similarity in their temperature dependence on the reaction rate. However, the re-reduced catalyst produced a steeper light-off curve reaching a maximum rate in CO_2 formation at 423 K. In fig. 2 the band positions of the dominant linearly bonded carbonyl species present on the catalyst surface during the reaction have been plotted against the catalyst temperature. Both plots show an initial period during which the stretching frequency was decreased followed by a period of invariance. For the fresh catalyst, the onset temperature for this invariance (2064 cm^{-1}) was at 423 K correlating with a temperature at which the rate of CO_2 formation was ca 75% of its maximum value. For the re-reduced catalyst, the onset temperature for invariance in the carbonyl stretching frequency (2076 cm^{-1}) was 388 K which correlates with a temperature where the rate of CO_2 formation was ca 10% of its maximum value. The position of the dominant carbonyl band for the re-reduced catalyst was consistently at higher frequencies than for the fresh catalyst. Fig. 3 shows infrared spectra of adsorbed CO recorded under reaction

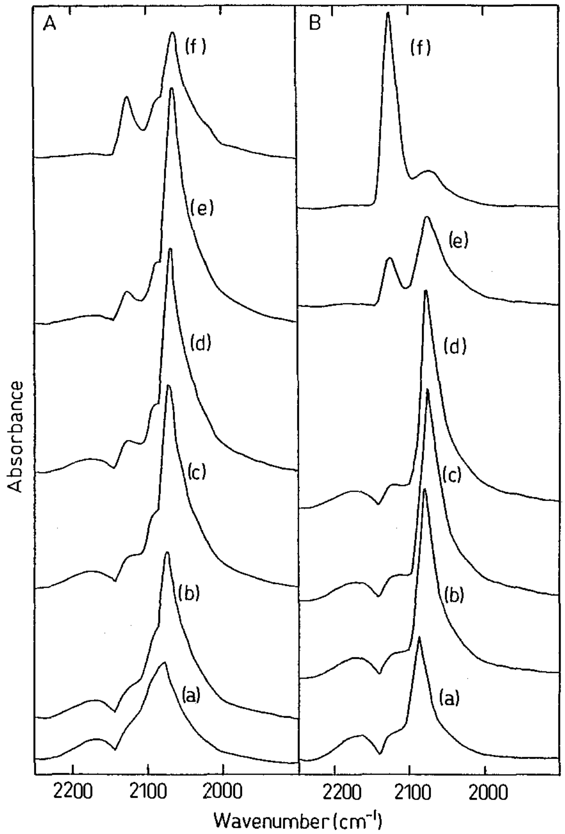

Fig. 3. Selected infrared spectra for Pt/Al_2O_3 catalyst (A) after primary reduction and (B) re-reduction, while heating (10 K min^{-1}) in a flow of CO(1%)/O_2(16%). Spectra recorded with the sample at (a) 303, (b) 248, (c) 373, (d) 398, (e) 423 and (f) 448 K.

conditions. For the fresh catalyst at 303 K, the form of the carbonyl bands is similar to spectra obtained by heating the catalyst in CO alone [7], with a central band at 2079 cm^{-1} and asymmetry at low (2025) and high (2090) frequencies. The latter was more clearly resolved at higher temperatures. In contrast, only one band assigned to linearly adsorbed CO was present for the re-reduced catalyst with a band maximum at 2087 cm^{-1} at 303 K. At higher temperatures, both series of spectra contained a band at 2125 cm^{-1} indicating CO adsorption on a more oxidised form of Pt [9,10].

4. Discussion

Spectra here for the fresh catalyst in CO/CO_2 are consistent with those previously reported for CO adsorption on well-dispersed Pt/Al_2O_3 with three linear carbonyl bands present [7,11–13]. As coupling will be less for CO adsorbed at sites of low coordination and on particles without extended terraces, the central linear carbonyl band may be assigned to adsorption at these sites whereas the high frequency shoulder may be attributed to adsorption at more extended terraces [11,13]. This high frequency shoulder for fresh catalyst (ca. 2090 cm^{-1} at 303 K) and the single band for the re-reduced sample (2087 cm^{-1} at 303 K) most likely indicate adsorption at a similar type of adsorption site. Possible assignments for the low frequency shoulder have been discussed [11,12]. The elimination of the lower frequency bands following re-reduction here would be consistent with the results of Sárkány and Gonzalez [12] where, according to the pretreatment procedure, a spectrum with one or three bands due to linearly adsorbed carbonyl species could be obtained. The sample with lower dispersion and displaying only one carbonyl band exhibited a higher CO oxidation activity [12].

Although the CO oxidation reaction over platinum is generally considered structure insensitive [2] and has been shown to exhibit no particle size dependence over a wide range of dispersions [14], it is possible that for very highly dispersed catalysts with particles containing a high proportion of step sites, a degree of structure sensitivity may be observed [12,15]. This higher specific activity for lower area Pt samples compared with high dispersed Pt samples is more likely to be observed in the range of low partial pressure of CO [15]. Similarly for the high O_2/CO ratio used here, although only marginal improvement in light-off was obtained for the re-reduced catalyst, the steeper curve indicating a higher relative activity at high percentage conversions would indicate an apparent structure sensitivity. The similarity between both activity profiles at low percentage conversions (fig. 1) would suggest that for both samples the light-off is determined by CO desorption from the weakest binding sites which are common to both catalysts. The steeper light-off profile for the re-reduced catalyst is more akin with the behavior exhibited by polycrystalline Pt wire than for a dispersed supported Pt catalyst [16]. As for Rh/Al_2O_3 [8], this is indicative of catalyst behavior following the annealing of particle surfaces and the reduction in the proportion of step and high index faces. Lower activity at higher conversions for the fresh catalyst compared with the re-reduced sample may be attributed to the lower reactivity of oxygen adsorbed at step sites relative to terraces [12,17,18] or due to inhibition as a result of strong adsorption of CO at these sites [11,15].

The observed invariance at 2076 cm^{-1} for the re-reduced catalyst is comparable with reported values of invariance at 2078 [4], 2081 [5] and 2090 cm^{-1} [6] during the CO oxidation reaction. These values would indicate that regionally high coverages of CO exist during the reaction and such large islands would demand reasonably extended terrace sites. Since maxima in plots in fig. 1 indicate complete conversion of CO in the gas flow, the duration of this invariance in the IR band for the re-reduced sample extends from ca. 10–100% CO conversion. Bands due to linearly adsorbed CO are observed for a period after 100% conversion is reached for both fresh and re-reduced catalysts, indicative of the low activity of these surface sites. In contrast with behavior for the re-reduced sample, the period of invariance at 2064 cm^{-1} for the fresh catalyst was maintained over a relatively short range of CO conversions (ca. 75–100%). Additionally for the same catalyst sample, it has been shown that this period of invariance fell within the same range of CO conversion regardless of the CO/CO_2 ratio in the range 1/1–35 and that the invariance always occurred at 2063-4 cm^{-1} [19]. Results here confirm a previous proposal [5] that isolated CO regions should be formed initially at extended low index crystalline faces rather than at the shorter terrace sites present on high index faces. The formation of these CO regions which result in invariance in νCO require the adsorption of oxygen followed by reaction on regions of the surface initially covered by CO. Since the initial CO desorption will dictate the ease with which this process may proceed, and this will occur more readily from the weaker binding extended close packed sites than from the stronger binding short terrace sites of the high index faces [11], the relative ease of formation of these regions on the two samples may be explained. As reported in previous studies [5–7] and as observed for the same sample as used in this study [19], heating of the catalyst in CO in the absence of oxygen leads to a monotonical decrease in the CO stretching frequency. For the fresh catalyst heated in the range 300–573 K, the band varied from 2080–2055 cm^{-1} [19]. Maintained values at 2064 cm^{-1} for the same catalyst in CO and oxygen would implicate a role of adsorbed oxygen in stabilising the adsorbed CO. One possibility is that by forming a strongly adsorbed row along step sites or other surface heterogeneity, adsorbed oxygen prevents the further movement of the oxygen front from reaching the adsorbed CO of the short terrace sites.

Particles may be envisaged as consisting of a series of short terraces separated by rows of step atoms and an extended terrace as the upper layer. During heating in CO/O_2, desorption and reaction results in the removal of adsorbed CO from this upper terrace allowing an oxygen front to move across the surface towards the step atoms. On reaching the step sites, reaction of the adsorbed CO and subsequent oxygen adsorption leaves a row of adsorbed oxygen atoms preventing further movement of the oxygen front. The trapped CO molecules remain on the lower terraces resulting in invariance in νCO. A degree of stability on this adsorbed CO may be supplied by these oxygen atoms at the step sites. Annealing of the particle surface by re-reduction leads to an extension of the terrace size and a reduction in the proportion of step atoms. For these particles, the oxygen front may move more readily over the extended terraces due to the relatively facile desorption of CO from these surfaces, allowing the oxygen front to reach the step atoms more readily (at a lower CO conversion value) than for the fresh catalyst. The trapped CO on the lower terraces of the re-reduced catalyst results in a higher frequency during the invariance as a result of the more extended nature of these sites on this catalyst. During invariance in νCO, reaction proceeds on the upper terrace devoid of the initially adsorbed CO. The residence time of CO adsorbed from the gas phase onto these sites will be short [21] and insufficient for its detection spectroscopically. This would be consistent with results of an IR study [5] which indicated that an undetected surface species was responsible for the catalytic activity (in this case during the period of νCO invariance). Elimination of the spectroscopically observed CO occurs at a higher temperature, and in this case, above the temperature at which 100% CO conversion in the flow is achieved [fig. 1,2].

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