Infrared spectroscopy and microcalorimetry studies of CO adsorption on sulfated zirconia supported platinum catalysts

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Carbon monoxide adsorption has been investigated on Pt particles supported on a high surface area zirconia and sulfated zirconias. The accessibility of the Pt surface determined from the comparison of H_2 chemisorption and transmission electron microscopy depends on two parameters: the temperature of treatment in air used to dehydroxylate sulfated zirconia, and the temperature of reduction. An oxidative pretreatment at 823 K yields a poor accessibility of Pt ($0.03 < H/Pt < 0.05$) whatever the temperature of reduction, whereas a Pt dispersion of 0.6 can be obtained by oxidation at 673 K followed by a mild reduction at 473 K. FTIR spectroscopy of adsorbed CO on Pt/ZrO_2 shows besides the normal linear species at 2065 cm^{-1}, a band at 1650 cm^{-1} which is attributed to CO bridged between Pt and Zr atoms. On Pt/ZrO_2–SO_4^{2-}, all bridged species tend to disappear, as well as the dipole–dipole coupling and ν_{CO} is shifted by 57 cm^{-1} to higher frequencies. These results are attributed to sulfur adsorption on Pt which decreases the electron back-donation from Pt to the $2\pi^*$ antibonding orbital of CO. The lower initial heat of CO adsorption observed on Pt/ZrO_2–SO_4^{2-} supports this proposal.

Keywords: sulfated zirconia; platinum; CO adsorption; IR spectroscopy; microcalorimetry

1. Introduction

There is a growing interest in sulfate-promoted zirconia as catalysts [1]. It has been claimed that sulfated zirconia develops very strong acidity with H_0 lower than -12 after calcination at 823 K [2], and is active at low temperature for the isomerization of light alkanes when promoted with platinum [3]. However, the state of platinum in Pt/ZrO_2–SO_4^{2-} catalysts is still controversial. From XPS and IR studies of adsorbed CO, Ebitani et al. [4] concluded that after calcination at 873 K and reduction at 523 K, platinum is mainly in the oxidized state, and that S^{2-} anions would not be associated with Pt. These conclusions, however, were questioned by Paal et al. [5]. In addition, Sayari and Dicko [6] from XPS, XRD and TPR studies claimed that Pt in Pt/ZrO_2–SO_4^{2-} was already reduced after calcination at 873 K and that reduction under hydrogen at 673 K did not change the state of Pt. The same conclusions were reached by Zhao et al. [7] from EXAFS experiments. Recently, however, results from Yori et al. [8] indicate that even after reduction at 573 K Pt supported on SO_4^{2-} is still in a non-metallic state.

The state of Pt is directly related with the severe conditions of activation needed to develop the strong acidity of sulfated zirconia. Indeed, the calcination step at high temperature and the subsequent reduction can lead to sintering and poisoning of the metallic phase. Therefore, the possible interaction of metallic particles with both strong acid sites and sulfur species can modify the Pt d-band.

On the other hand, acidity of medium strength could be also required, and this could be attained by dedicated thermal treatments of ZrO_2–SO_4^{2-}. It was, therefore, the aim of this work to investigate the effect of some moderate thermal treatments of the properties of platinum in Pt/ZrO_2–SO_4^{2-} catalysts. Special attention was paid to the size of the Pt particles, the accessibility to the metal site and electronic state of Pt. This was achieved using transmission electron microscopy, hydrogen chemisorption, FT-IR spectroscopy and calorimetry of CO adsorption.

2. Experimental

2.1. Reactants and catalysts

The catalysts were prepared by using γ-Al_2O_3 (Rhône Poulenc, GSFC-200), H_2PtCl_6 (Interchim, 38% Pt, purum grade), $ZrOCl_2 \cdot 8H_2O$ (Fluka, purity $> 99.0\%$) to prepare the parent zirconium hydroxide, and a precalcined sulfated zirconia (MEL Chemicals, XZ.0707). This zirconia was calcined at 873 K for 1 h at the plant. It contains also 6% Al, used as a binder for the preparation of the extrudates.

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Pt/Al$_2$O$_3$. The amount of H_2PtCl_6 required to obtain a 1% Pt catalyst was dissolved in 10 cm^3 of deionised water per gram of support. The alumina was immersed in the solution for 5 h at pH ≈ 2. After filtration, the solid was first dried at 393 K before calcination at 623 K for 4 h, and reduction at 473 K for 4 h with diluted H_2 (H_2/N_2: 20/80, heating ramp: 1 K min^{-1}).

Pt/ZrO$_2$. Zirconium hydroxide was prepared by hydrolysis of $ZrOCl_2$ with concentrated ammonia. The reactants were added dropwise within 3 h and the pH was kept constant at 10. The gel was allowed to mature for 6 h before filtration and washing until pH = 7 and no more chloride was detected in the washing solution. The procedures for introducing Pt and for the subsequent thermal treatments were the same as described above.

Pt/ZrO$_2$–SO$_4^{2-}$. This catalyst was prepared starting from the home-made zirconium hydroxide described above. Sulfation was performed using 0.1 N sulfuric acid (15 ml/g of support). The zirconium hydroxide was immersed in the sulfation solution for 5 h. After drying at 393 K, platinum was introduced by dry impregnation using an aqueous solution of H_2PtCl_6. After drying at 393 K, the solid was calcined at 673 K for 4 h and subsequently reduced at 473 K for 4 h in diluted H_2 (H_2/N_2: 20/80, heating ramp: 1 K min^{-1}).

Pt/ZrO$_2$–SO$_4^{2-}$ MEL. The procedure for metal deposition and the thermal treatments were the same as described above for catalyst $Pt/ZrO_2–SO_4^{2-}$. The extrudates were then ground in a mortar.

2.2. Characterization

Chemical analyses of the samples, by atomic absorption after dissolution of the samples, were performed at the Service Central d'Analyse du CNRS (Solaise, France). The size of the metallic particles was determined by transmission electron microscopy using a Jeol 100CX microscope and the carbon replica technique. Hydrogen chemisorption was measured in a conventional static apparatus. Before each experiment, the sample (~ 300 mg) was reactivated in situ by reduction at 473 K for 4 h under H_2, then evacuated at 473 K for 2 h at a pressure of 2×10^{-4} Pa. The hydrogen pressure in equilibrium with the catalyst was measured at room temperature in the range 1.3–20 kPa. The hydrogen uptake was estimated by the extrapolation to zero pressure of the linear part of the isotherm.

The reducibility of Pt catalysts after calcination was characterised by temperature-programmed reduction by hydrogen (TPR). An aliquot of the catalyst (~ 200 mg) was activated first at 673 K for 1 h under flowing air at 100 cm^3 min^{-1}. The sample was cooled to room temperature under a He flow (20 cm^3 min^{-1}), this was replaced by the reducing H_2/Ar gas (3/97, vol/vol), and the temperature was raised at 5 K min^{-1} from 293 to 673 K (flow: 20 cm^3 min^{-1}). The H_2 uptake was monitored with a thermal conductivity detector, and the nature of the exit gases by a quadrupole mass spectrometer (Balzers QMS421). The purity of all gases used was > 99.995%.

CO adsorption was studied by diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) using a Biorad FTS-40 Fourier transform infrared instrument equipped with diffuse reflectance optics and environmental cell (Spectratech Ltd.) [9]. The catalyst (~ 150 mg) was first, dried, in situ, at 473 K in He (BOC Ltd., 99.996%) which was purified by passage through a number of traps: Cu turning at 473 K, activated charcoal, high capacity and indicating oxy traps (Alltech Ltd.) and two molecular sieve traps at 298 and 77 K. The sample was then treated under H_2 (30 cm^3 min^{-1}) for 30 min at 473 K and outgassed under He flow (20 cm^3 min^{-1}) for 2 h. After cooling to room temperature, small amounts of CO (Linde Gas, 99.97%) were pulsed to a six-way sampling valve. Temperature-programmed desorption (TPD) spectra were recorded in situ as the sample was heated to 473 K at ca. 15 K min^{-1} in flowing He.

Heats of CO adsorption were determined with a modified SETARAM microcalorimeter DSC-111, the flowing gas passes through the bed of catalyst (5–10 mm height) inside a silica reactor, which is placed in the calorimetric cell. The sample was first activated by H_2 treatment at 473 K, and after outgassing under flowing He (20 cm^3 min^{-1}) at this temperature was cooled to room temperature when 1–3 μmol of CO were pulsed to the catalyst using a six-way sampling valve flushed with He. The thermal event in the calorimetric cell was recorded as a function of the CO uptake, which is monitored by a catharometer. All the gases were of ultra high purity and further purified by molecular sieve and MnO traps.

The main characteristics of the catalysts are given in table 1. This table shows that after calcination at 673 K, $Pt/ZrO_2–SO_4^{2-}$ exhibits a higher S_{BET} than Pt/ZrO_2. This is due to the stabilizing effect of SO_4^{2-} against phase transformation [2]. The lowest S_{BET} value of $Pt/ZrO_2–SO_4^{2-}$ MEL is the result of the higher calcination temperature (873 K) applied for the preparation of this sample.

3. Results

It is of interest to comment first on the data for the Pt/Al_2O_3 and Pt/ZrO_2. Table 1 presents the mean Pt particle size derived from TEM and H_2 chemisorption. For unpoisoned supported Pt particles, there is an empirical relationship between the mean particle size (dp) and Pt dispersion (H/Pt), dp(nm) $\approx$ 1/(H/Pt). The agreement is excellent for Pt/Al_2O_3, but not for Pt/ZrO_2. This behaviour is similar to that reported for Ru-based catalysts when supported on high surface area amorphous zirconia, but not on crystalline zirconia [10].

Table 1
Main characteristics of the catalysts, after calcination at 673 K and reduction at 473 K

Catalysts	S_{BET} ($m^2 g^{-1}$)	wt% S	wt% Pt	H/Pt	Mean particle size (nm) from	
					TEM	H_2 chem.
Pt/Al_2O_3	205	0	1.0	0.86	1.5	1.2
Pt/ZrO_2	195	0	1.0	0.22	1.5	4.5
$Pt/ZrO_2–SO_4^{2-}$	270	2.6	1.5	0.59	1.6	1.7
$Pt/ZrO_2–SO_4^{2-}$ MEL	125	3.8	1.2	0.31	1.2	3.2

It was suggested that Zr^{n+} or ZrO_x species decorated the Ru particles, then decreasing the H_2 uptake. This phenomenon was not initiated during the low temperature reduction step (< 673 K) as in the so-called SMSI effect, but probably during the impregnation/deposition step of the precursor [11].

The $Pt/ZrO_2–SO_4^{2-}$ was submitted to different thermal treatments with calcination for 4 h under air with temperature ranging from 673 to 823 K, and reduction for 4 h under diluted H_2 (H_2/N_2: 20/80, heating ramp: 1 K min^{-1}) with temperature ranging between 473 and 573 K. Fig. 1a shows the Pt accessibility (H/Pt) as a function of calcination and reduction temperatures. One can see that, whatever the nature of the thermal treatment, the Pt accessibility decreases when the temperature increases.

On the other hand, the protocol for H_2PtCl_6 introduction has an influence on the extent of H_2 chemisorption on the Pt surface. Table 1 presents the H/Pt value and the mean particle size of Pt for two samples activated under the same conditions (calcination at 673 K, reduction at 473 K) but impregnated with H_2PtCl_6 at different stages. $Pt/ZrO_2–SO_4^{2-}$ was prepared by impregnation of H_2PtCl_6 on sulfated zirconium hydroxide followed by the thermal treatment; $Pt/ZrO_2–SO_4^{2-}$ MEL was prepared by impregnation of sulfated zirconia precalcined at 873 K with H_2PtCl_6 followed by the thermal treatment. The extent of inhibition of the Pt surface is higher in the latter sample which contains also a higher density of sulfur species. The properties of poisoned and unpoisoned Pt particles supported on $Pt/ZrO_2–SO_4^{2-}$ and reduced at 473 K have been studied by

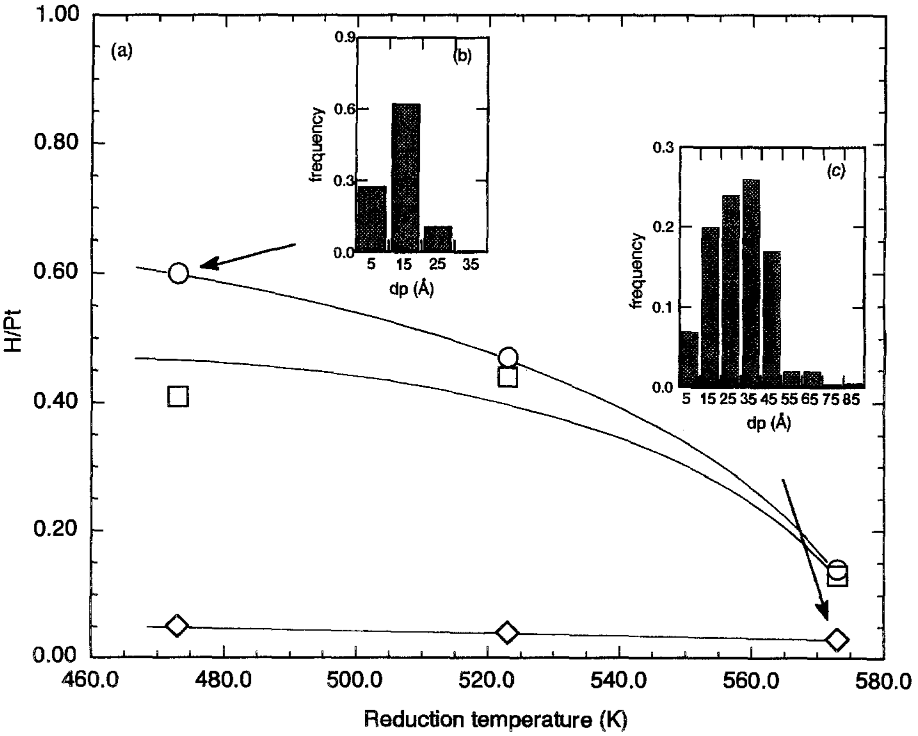


Fig. 1. (a) Hydrogen uptake on $Pt/ZrO_2–SO_4^{2-}$ as a function of reduction temperature after calcination at (○) 673 K, (□) 773 K, and (◇) 823 K. (b) Distribution of Pt particle size in $Pt/ZrO_2–SO_4^{2-}$ after calcination at 673 K and reduction at 473 K. (c) Distribution of Pt particle size in $Pt/ZrO_2–SO_4^{2-}$ after calcination at 823 K and reduction at 573 K.

adsorption of CO followed by IR spectroscopy and calorimetry.

The IR spectra of CO adsorbed on Pt catalysts are shown in fig. 2. For each sample the CO spectra at room temperature are presented after introducing CO, at low coverage, at saturation and after heating to 473 K. For all the samples, there is a main absorption band in the range 2100–2000 cm^{-1} which corresponds to linearly adsorbed CO on Pt, and minor contributions between 2000 and 1600 cm^{-1}, usually assigned to bridged CO species.

The first point to emphasize is that, in contrast to the findings of Ebitani et al. [4] who did not observe any absorption band in the 1900–2100 cm^{-1} spectral region on sulfated Pt/ZrO_2, there is very clear evidence of CO adsorption on the present sulfated samples. However, it is worth noting that the catalysts were submitted to different thermal treatments: Ebitani et al. [4] introduced Pt as H_2PtCl_6 on $Zr(OH)_4$ before the calcination step at 873 K, whereas we introduced Pt as H_2PtCl_6 in aqueous solution on the sulfated zirconium hydroxide, or sulfated

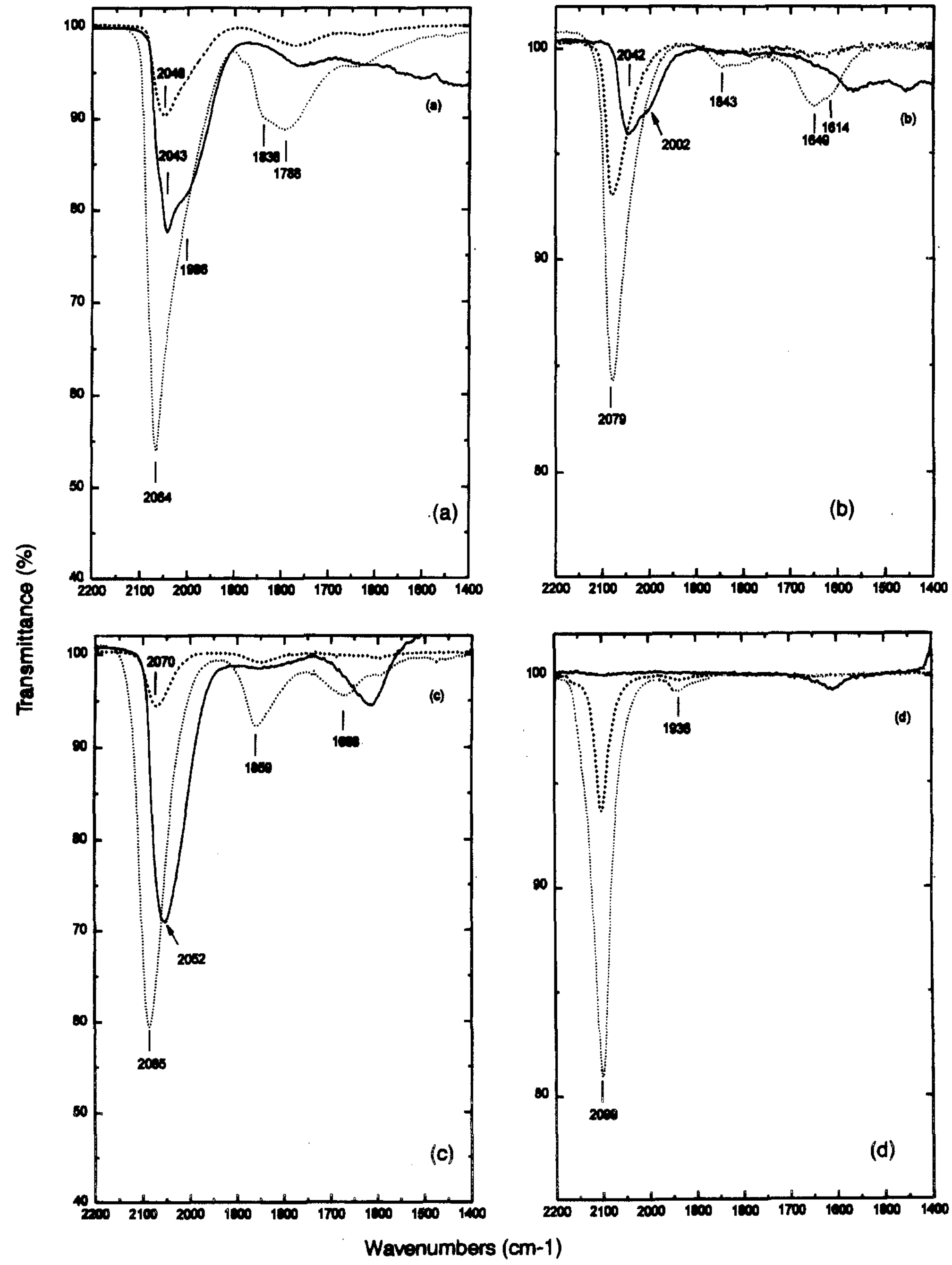


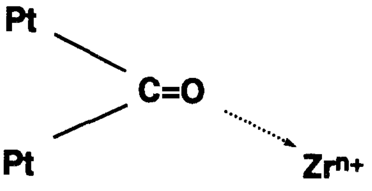
Fig. 2. Infrared spectra of CO adsorption on (a) Pt/Al_2O_3, (b) Pt/ZrO_2, (c) $Pt/ZrO_2–SO_4^{2-}$, (d) $Pt/ZrO_2–SO_4^{2-}$ MEL; (...) after 1 μmol CO pulse ($\theta \approx 0.1–0.3$) (---) at full CO coverage, (——) after heating and evacuation at 473 K.

zirconia previously calcined at 873 K, the solid being then calcined at only 623 K.

Upon heating to 473 K, the bridged CO species disappear first, in agreement with literature [12–14]. However, if we consider the intensity of the main component, i.e. the linearly adsorbed CO, the behaviour between Pt/Al_2O_3 and $Pt/ZrO_2–SO_4^{2-}$ MEL is quite different. On the former, there is only a 50% intensity decrease on heating, whereas the band totally disappears on the latter. Also, except for $Pt/ZrO_2–SO_4^{2-}$ MEL, as the samples are heated to 473 K, the CO coverage decreases with a concomitant shift of ν_{CO} to lower frequency. This red shift is classically explained by the decrease of dipole–dipole coupling between neighbouring adsorbed CO. In contrast, there is no shift of the ν_{CO} in $Pt/ZrO_2–SO_4^{2-}$ MEL, which remains at a high value, around 2100 cm^{-1}.

After these general observations, we focussed our attention on each sample more precisely. The adsorption of CO on Pt/Al_2O_3 has been widely studied and the results we have obtained on this sample of high Pt dispersion are in good agreement with literature data. In short, there are at least three contributions of linearly adsorbed CO in the 2100–2000 cm^{-1} spectral zone: the wavenumbers of these bands take the approximate values of 2065, 2045 and 1995 cm^{-1} after heating to 473 K. These values agree well with those reported by Kappers et al. [15] for CO adsorption on a Pt/Al_2O_3 of a similar dispersion. These contributions would correspond to CO adsorbed on Pt(100), Pt edge atoms and Pt corner atoms respectively. On the other hand, the broad band between 1900 and 1750 cm^{-1} is likely to be constituted of two contributions which occur at around 1850 and 1800 cm^{-1}, this would correspond to twofold and threefold CO bridged species on Pt(100) respectively [13].

The CO IR spectra found on Pt/ZrO_2 differ appreciably from those on Pt/Al_2O_3. In the linearly adsorbed CO region, it seems that only two contributions occur at 2042 and 2002 cm^{-1}. On the other hand, the bands between 1900 and 1750 cm^{-1} corresponding to bridged CO species are very small. This is in agreement with the presence of Zr^{n+} or ZrO_x species on the Pt particles, as discussed above, which tend to isolate Pt^0 sites, thus decreasing the probability of bridging CO species. Another clear difference with respect to Pt/Al_2O_3 is the appearance of a new absorption band at 1650 cm^{-1}. The adsorption of CO on zirconia-supported metals is not well documented. Gugliominotti [16] reported the occurrence of a broad band centered at 1660 cm^{-1} for the CO adsorption on Rh/ZrO_2. This component was assigned to CO species bonded at the borderline of Rh^0 particles through the C atom but also bridge-bonded to the coordinatively unsaturated Zr^{4+} or Zr^{3+} ions through the O atom. We have tentatively assigned the band we have found at 1650 cm^{-1} to a similar bridge-bonded CO species (scheme 1).



Scheme 1.

The IR spectra of CO adsorbed on sulfated Pt/ZrO_2 differ markedly from the others, although the $Pt/ZrO_2–SO_4^{2-}$ exhibits an intermediate behaviour between Pt/ZrO_2 and $Pt/ZrO_2–SO_4^{2-}$ MEL. The first point which deserves a comment is the increase of bridged CO species, at 1859 cm^{-1}, on $Pt/ZrO_2–SO_4^{2-}$ compared to Pt/ZrO_2. It was said above that ZrO_x moieties on the Pt particles were responsible for the low Pt accessibility and for the decrease of bridged CO species. Thus, the sulfation of $Zr(OH)_4$ prevents the decoration of Pt particles during the impregnation/deposition step of the precursor. CO adsorption on $Pt/ZrO_2–SO_4^{2-}$ MEL proves to be particularly interesting. First of all, as previously mentioned, CO desorbs easily upon evacuation at 473 K, which is evidence of a weak bond between CO and Pt. However, Pt is very likely to be in a zerovalent state even though there is a blue shift of the frequency to the high value of 2099 cm^{-1}. As pointed out earlier, this is very difficult from the findings of Ebitani et al. [4] who did not find any absorption band of CO on sulfated Pt/ZrO_2. The main component of the IR spectra on $Pt/ZrO_2–SO_4^{2-}$ MEL is the linearly adsorbed CO band at 2099 cm^{-1}, which is not shifted to lower wavenumbers upon CO desorption. The behaviour of this band reflects (i) a lower back donation from the d-electron of Pt to the $2\pi^*$ antibonding CO orbital which increases the ν_{CO} frequency, (ii) the absence of the dipole–dipole coupling whatever the CO coverage. Finally, the contribution due to bridged CO species is very small and is shifted to higher frequency by about 70 cm^{-1} too.

The energetics of CO adsorption on Pt has been studied by microcalorimetry. Fig. 3 presents the differential heats of CO adsorption on Pt/Al_2O_3, and $Pt/ZrO_2–SO_4^{2-}$ MEL catalysts as a function of CO coverage. The initial heat of CO adsorption on Pt/Al_2O_3 is higher than the reported values of 134 kJ mol^{-1} on Pt/TiO_2 [17], and of 140 kJ mol^{-1} on Pt/SiO_2 [18]. By contrast, the initial heat of CO adsorption on $Pt/ZrO_2–SO_4^{2-}$ MEL is lower by 25 kJ mol^{-1}. As a consequence of the lower heat of adsorption the CO from this sample is fully desorbed by heating to 473 K, as shown by the IR spectra (fig. 2d). This allowed a TPD spectrum to be constructed from the spectra collected as the sample was heated to this temperature and the rate of CO desorption proved to be at a maximum at 428 K, which, on using Redhead's method [19], corresponds to a desorption energy of 129 kJ mol^{-1}, in reasonable agreement with the results from microcalorimetry.

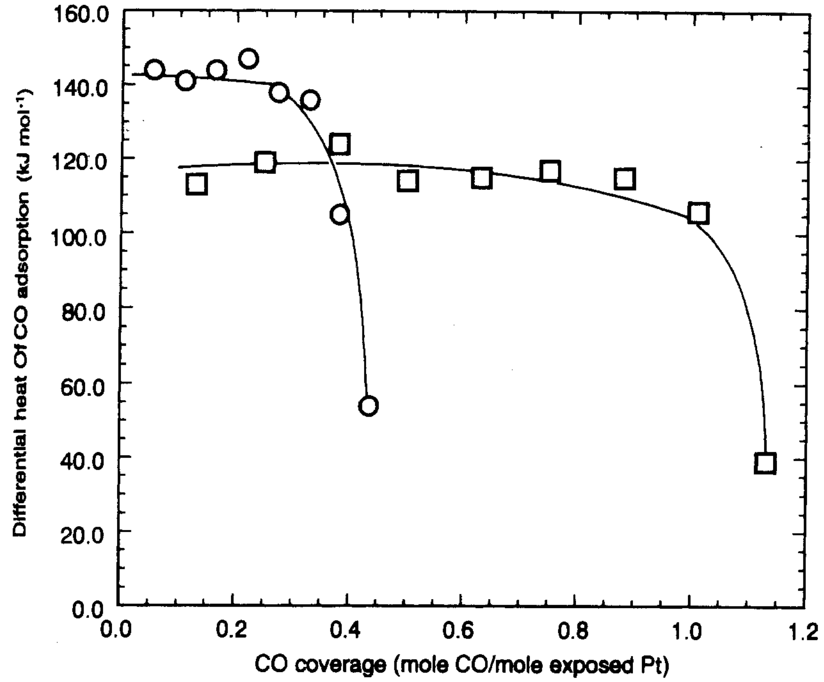


Fig. 3. Differential heat of CO adsorption on (○) Pt/Al_2O_3, and (□) Pt/ZrO_2–SO_4^{2-} MEL at 313 K.

4. Discussion

We focus mainly on the behaviour of sulfated Pt/ZrO_2. First of all, the question is raised about the nature of the decrease of H/Pt upon the severity of the thermal treatments applied to Pt/ZrO_2–SO_4^{2-}; is it a sintering or a poisoning of the metallic phase? Figs. 1b and 1c present the Pt particle size distributions, determined by TEM, for Pt/ZrO_2–SO_4^{2-} after two different thermal treatments. It comes out that: (1) after calcination at 673 K and reduction at 473 K, the mean particle size (~ 1.5 nm) merely corresponds to that deduced from H_2 chemisorption, then the extent of poisoning of the Pt particles is very likely limited; (2) the strong decrease of Pt accessibility after calcination at 823 K is mainly due to poisoning, and by sintering to a much lesser extent, since the mean particle size deduced from H_2 chemisorption is ten times larger than that determined from TEM. The same Pt accessibility (H/Pt ≈ 0.03, after calcination at 823 K and reduction at 573 K) was reported by Iglesia et al. [20] after activation of a Pt/ZrO_2–SO_4^{2-} under similar conditions. This poisoning of Pt during the calcination step might occur through migration of SO_x species onto Pt particles. Part of these species could be further reduced to sulfide during the reduction step. This is supported by the TPR experiments carried out on Pt/Al_2O_3, Pt/ZrO_2–SO_4^{2-} and ZrO_2–SO_4^{2-} (fig. 4). In the absence of Pt, ZrO_2–SO_4^{2-} is hardly reducible, and not before 800 K. By contrast, Pt particles greatly help the reduction of sulfoxide species which starts from 570 K, after reduction of PtO_x particles. The reduction of SO_x species was confirmed by the parallel release of H_2S detected by mass spectroscopy after 670 K. Some of the H_2S will thus interact with Pt^0 to give Pt–S. Release of H_2S during thermal treatment of $H_2PtCl_6/Zr(OH)_4SO_4^{2-}$ under H_2/He was also observed after 673 K [21]. From XPS studies of sulfated Pt/ZrO_2, Ebitani et al. [4] showed that 10% of SO_4^{2-} would be reduced to S^{2-} at 573 K. However, they do not consider that S^{2-} interacts with Pt. On the other hand, due to the larger size of the Pt particles, Zhao et al. [7] could not conclude to the presence of adsorbed S^{2-} when studying sulfated Pt/ZrO_2 by EXAFS. Nevertheless, it seems difficult to establish directly that sulfur is in contact with Pt, but simple calculations show that no more than

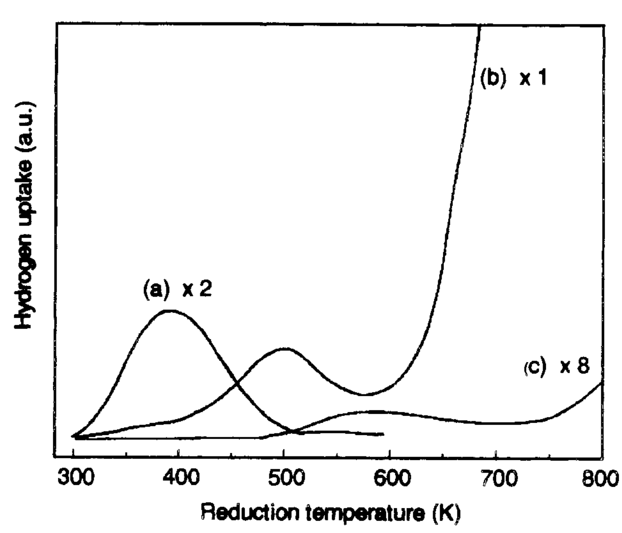


Fig. 4. Temperature-programmed reduction by hydrogen of (a) Pt/Al_2O_3, (b) Pt/ZrO_2–SO_4^{2-} and (c) ZrO_2–SO_4^{2-}.

0.05% S (2–4% of the sulfur content of the sample) is sufficient to poison all the Pt sites, and would certainly escape detection in XPS analysis. Finally, the lower reducibility of $Pt/ZrO_2-SO_4^{2-}$ in comparison with Pt/Al_2O_3 should be pointed out.

If one assumes now that sulfur is partially poisoning the Pt surface, the consequences on the CO will be the following:

(1) Sulfur being an electrophilic adsorbate like oxygen, the "co-adsorption" of sulfur with CO will decrease the back-donation of a Pt d-electron to the $2\pi^*$ antibonding orbital. Thereby a blue shift of all the ν_{CO} frequencies will result [12,22] as well as a weaker bonding between CO and Pt [23].

(2) According to Biloen et al. [24], poisoning of the Pt surface by sulfur occurs at random, which induces a dilution, or isolation, of the Pt atoms. The consequence of this isolation of Pt^0 sites on CO adsorption will be the following: (i) a decrease of bridged CO species which need several neighbour and bare Pt atoms to occur, (ii) the disappearance of dipole–dipole coupling between CO adsorbed molecules, then the constancy of the ν_{CO} frequency as the CO coverage decreases.

The studies of CO adsorption on $Pt/ZrO_2-SO_4^{2-}$ MEL by IR and calorimetric experiments (figs. 2 and 4) clearly show that the phenomena mentioned above are indeed observed: (i) a blue shift of the ν_{CO} frequency of linearly adsorbed CO from 2042 to 2099 cm^{-1}, (ii) the disappearance of CO bridged species, (iii) the constancy of the ν_{CO} frequency upon heating at 473 K (low CO coverage), (iv) a lower heat of CO adsorption. It emerges that the hypothesis of a Pt particle poisoned by sulfur is well supported by the CO adsorption studies. Otherwise, a shift to a higher ν_{CO} frequency could also be induced by the acidity of the sulfated ZrO_2. Actually, if such a shift exists, it is superimposed with that induced by S co-adsorbate and seems difficult to extract. We can only remark that a blue shift of ν_{CO} from 2080 to 2095 cm^{-1} upon sulfation of Pt in Pt/Al_2O_3 catalysts was reported [22,25]. On the other hand, by studying CO adsorption on Pt/HNaY, Samant and Boudart [26] observed a shift from 2060 to 2079 cm^{-1} of ν_{CO} ($\theta \approx 0.15$) when increasing the acidity of the zeolite. If we compare Pt/ZrO_2 and $Pt/ZrO_2-SO_4^{2-}$ MEL, we observe a blue shift of 48 cm^{-1} at low CO coverage. May be this high $\Delta\nu_{CO}$ is due to the cooperative effect of adsorbed sulfur on Pt and of sulfated-ZrO_2 acidity.

5. Conclusions

$Pt/ZrO_2-SO_4^{2-}$ catalysts treated under severe conditions (calcination at 823 K, reduction at 573 K) show very low accessibility of Pt. This is mainly due to poisoning by sulfur of the Pt surface, and to sintering to a much lesser extent. The decrease of accessibility starts after calcination at 773 K and/or reduction at 573 K. The Pt atoms of the S poisoned surface layer are reduced but exhibit strong electronic modifications which are put in evidence by an upward shift by 48 cm^{-1} of ν_{CO} of linearly adsorbed CO species and a decrease by 25 kJ mol^{-1} of the heat of CO adsorption compared to Pt/Al_2O_3. This phenomenon is attributed both to the electron-withdrawing effect of adsorbed sulfur, and of the acidity introduced by sulfate anions.

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