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Influence of the strong metal–support interaction on the CO chemisorption at a Pt / SiO_2 catalyst

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Pt / SiO_2 catalysts prepared by sol–gel processing were studied by transmission electron microscopy, electron diffraction, high-resolution electron microscopy and Fourier-transform infrared spectroscopy. The samples exhibit uniform dispersion of the metal phase with narrow particle size distribution. Treatment with hydrogen in the temperature range 773–923 K yields Pt / Si alloys at lower temperatures and platinum silicides (Pt_3Si and $Pt_{12}Si_5$) at higher temperatures. The CO chemisorption shows that with increasing degree of alloying (1) the $\nu(CO)_l$ and the $\nu(CO)_b$ band shifts to lower wavenumbers, (2) the intensity of the $\nu(CO)_l$ band decreases and (3) the $\nu(CO)_b / \nu(CO)_l$ intensity ratio increases. The phenomena are interpreted by simultaneous effects of Pt surface dilution, enhanced electron back-donation from platinum to CO and Pt d-band narrowing.

Keywords: silica-supported platinum, sol–gel processing, strong metal–support interaction, FTIR-spectroscopy, electron microscopy, electron diffraction

1. Introduction

During the last decade the sol–gel process has received much attention in research and application [1–6]. It offers many advantages as compared to the conventional routes like impregnation or coprecipitation, i.e., a better control of content and distribution of the metal and a higher thermal stability of the metal dispersion since sintering processes are impeded due to the encapsulation of the metal in the rigid porous silica framework. The activity of catalysts can be affected by poisoning of the active component, sintering or interaction of the metal with the support. The latter, caused by a strong metal–support interaction (SMSI), has been found for transition metal oxides such as TiO_2 [7] and even for non-transition metal oxides such as SiO_2 [8,9], Al_2O_3 [10,11] and MgO [12]. It has been shown that reduction of such catalysts above a critical temperature results in a marked suppression of hydrogen and carbon monoxide chemisorption capacity at room temperature. Oxidation followed by hydrogen reduction at temperatures below the critical one, usually, restored the sorption properties of the catalyst.

This paper reports on the formation of Pt_3Si and $Pt_{12}Si_5$ by high-temperature reduction of the Pt / SiO_2 catalyst. The influence of the strong metal–support interaction on the CO chemisorption was investigated. By means of electron diffraction the observed changes in chemisorption behavior will be correlated to the microstructure.

2. Experimental

The sample Pt / SiO_2 (1.6 wt%) was prepared by sol–gel processing. Details of the procedure have been described previously [5,6]. Before investigating the samples by electron microscopy and Fourier-transform infrared (FTIR) spectroscopy they were reduced in a quartz reactor in a flow of dried hydrogen (6 ℓ/h, Messer-Griesheim 99.999% purity). The reduction was performed at several temperatures between 773 and 923 K for 10 h. The sample reduced at 923 K was oxidized in an oxygen atmosphere (Messer-Griesheim 99.995% purity) at 623 K for 1 h in situ in the FTIR spectrometer.

All specimens were examined in a Philips EM 420 and a Philips CM 20 transmission electron microscope (TEM) operated at 120 and 200 kV, respectively. The catalysts were ground to a fine powder and deposited on a copper grid coated with a carbon film.

The FTIR spectra were obtained with a resolution of 2 cm^{-1} on a single-beam spectrometer (BIO-RAD FTS 60 A) where the samples were mounted in a heatable UHV-cell. Before recording the samples were evacuated overnight, then exposed to 6 mbar CO (Messer-Griesheim, 99.995% purity) and again evacuated.

3. Results

3.1. FTIR spectroscopy

Fig. 1 (solid lines) shows the influence of the reduction temperature on the CO chemisorption. The spectrum of

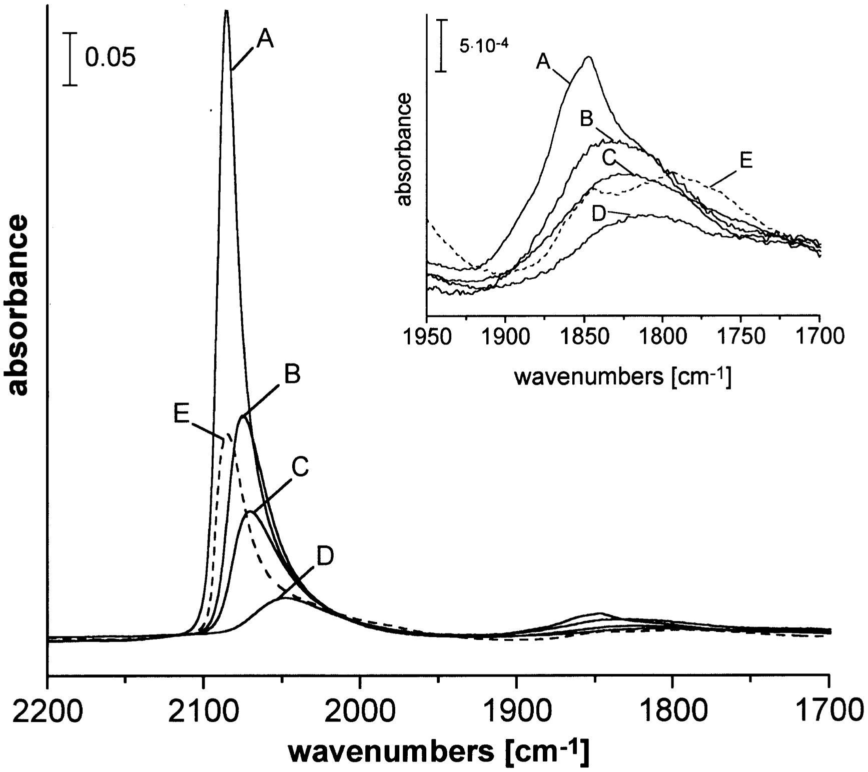

Fig. 1. Infrared spectra of CO chemisorbed on Pt/SiO_2 at room temperature following (i) reduction treatments with hydrogen (0.1 MPa) at 773 (A), 823 (B), 873(C) or 923 (D) K, and (ii) regeneration of sample D by oxidation (O_2, 20 kPa) at 623 K and subsequent reduction (H_2, 20 kPa) at 773 K (E).

the sample reduced at 723 K (A) is typical for metallic platinum on which CO favours the single-atom position due to the relatively large d-bandwidth [13]. The strong and narrow band at 2086 cm^{-1} (HFB = high-frequency band) is assigned to linear CO and the weak and broad band at 1850 cm^{-1} (LFB = low-frequency band) to the bridge-bonded CO [14]. Relatively large BET values (> 300 m^2/g) showed a high porosity and, thus, a good accessibility of the metal particles for gas molecules. Reduction at temperatures higher than 773 K caused a marked decrease in the intensity of both CO bands (spectra B–D) whereas the $\nu(CO)_b/\nu(CO)_l$ intensity ratio increased. Additionally, the HFB and LFB shifted to lower wavenumbers (table 1).

Oxidation in situ at 623 K and subsequent reduction at 673 K of the sample previously reduced at 923 K resulted in a partial regeneration of the CO chemisorption properties (fig. 1, spectrum E, dashed line). The additional band at 1790 cm^{-1} cannot be interpreted up to now, but possibly it may be attributed to a three-fold bonded CO species.

Table 1
Shift of the linear- (CO_l) and bridge-bonded (CO_b) CO bands on Pt/SiO_2 in dependence on the reduction temperature

Reduction temp. (K)	CO_l (cm^{-1})	CO_b (cm^{-1})
773 (A)	2086	1848
823 (B)	2075	1830
873 (C)	2069	1825
923 (D)	2048	1810

3.2. Electron microscopy

Reduction at temperatures up to 873 K for 10 h led to Pt particles with an average size of 4 nm, which was evaluated with standard deviations of 5% (fig. 2). Electron diffraction analysis showed diffraction rings characteristic for metallic platinum. Reduction at temperatures higher than 873 K for 10 h caused a change in chemical composition and particle shape. Electron diffraction analysis showed the presence of diffraction rings of metallic platinum and, additionally, of diffraction rings of Pt_3Si and $Pt_{12}Si_5$ (table 2). The average particle size has not increased markedly, i.e. from 4 to 5.2 nm, but some particles with diameters above 10 nm were observed. High-resolution electron microscopy (HREM) studies of this sample revealed elongated particles wetting the surface of the silica support (fig. 3). The visible interplanar spacings $d = 0.221$ nm belong to Pt_3Si. Oxidation at 623 K for 1 h resulted in a destruction of the platinum silicides and a disappearance of the elongated particles.

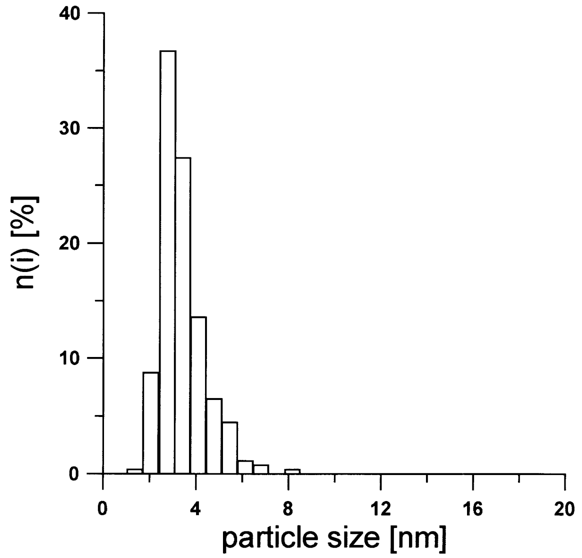

Fig. 2. Particle size histogram of Pt/SiO$_2$ after reduction at 773 K.

4. Discussion

TEM micrographs of the prepared samples demonstrated, that the sol–gel process and the subsequent reduction resulted in uniform platinum dispersions. The small increase of the mean Pt crystallite size upon increase of the reduction temperature from 773 to 923 K indicated a moderate sintering, presumably due to Ostwald ripening since no indication of migration and coalescence was observed. The shape of the size histograms (fig. 2), exhibiting a tailing to larger particle sizes, confirmed the assumption.

Reduction at temperatures higher than 773 K caused a strong decrease of the chemisorption capacity for CO on Pt/SiO$_2$ (fig. 1, solid lines), which is not due to the sintering of metal particles in consequence of the thermal treatment. Since electron diffraction analysis of the sample reduced at 923 K showed diffraction rings of metallic platinum and additional rings of Pt_3Si and $Pt_{12}Si_5$ (table 2) the decrease of the CO chemisorption capacity can be attributed to the appearance of silicides. Though the electron diffraction revealed both metallic platinum and silicide phases the corresponding CO band of metallic platinum (2086 cm^{-1}) is absent but a new band appeared at 2048 cm^{-1} (fig. 1, spectrum D). The oxidation of this sample at 623 K resulted in a disappearance of the silicides, a recovery of the band at 2086 cm^{-1} and a partial regeneration of the chemisorption capacity. Obviously, a reversible strong metal–support interaction (SMSI) in the Pt/SiO$_2$ system from the sol–gel process resulted in the formation of platinum silicides as found previously for impregnated Pt/SiO$_2$ systems [8,9].

Table 2
Measured interplanar distances d (nm) from electron diffractograms of Pt/SiO$_2$ heated at 923 K in H_2 in comparison with interplanar distances found in the literature

Pt_3Si		Measured d (nm)	$Pt_{12}Si_5$	
(*hkl*)	d (nm)		d (nm)	(*hkl*)
		0.591	0.590	101
		0.347	0.348	301
		0.299	0.301	420
202	0.2779	0.278		
202	0.2691	0.268		
113	0.2317	0.232		
		0.211	0.2111	412
		0.192	0.1929	432, 502
		0.182	0.1820	103
040, 004	0.1939	0.194		
333	0.1473	0.148		
440	0.1365	0.137		

The samples reduced at 823 and 873 K showed similar changes of the chemisorption properties as the silicide sample (923 K), but electron diffraction revealed only metallic platinum. It is likely that these effects are due to an initial state of the SMSI, which cannot be detected by electron diffraction.

The characteristic features of the chemisorption behavior of all samples are (i) a shift to lower wavenumbers (table 1) and (ii) a marked decrease in the total absorption intensity whereas the $\nu(CO)_b/\nu(CO)_l$ intensity ratio increases from 0.1 at 773 K to 0.5 at 923 K. An interpretation of the obvious correlation between the Pt state and the CO chemisorption is attempted as follows. Alloying of Pt with Si alters the electronic and geometric properties of the surface. With regard to segregation in bimetallic systems the enrichment of the surface of the particles with one element has to be considered. In the system Pt/Si it is expected that silicon, having the lower heat of sublimation, segregates to the surface [15,16]. This dilution of the platinum surface with silicon atoms separates the chemisorbed CO molecules and decreases the dipole–dipole coupling resulting in a shift to lower wavenumbers (geometric or ensemble effect). It has been found that the full shift from the singleton frequency on platinum at 2060 cm^{-1} [17] to higher frequencies with increasing CO coverage can be attributed to the dipole–dipole coupling [18]. The observed shift of the HF-band to 2069 cm^{-1} (spectrum C in fig. 1) may be caused by both dilution of the platinum surface with silicon atoms as well as by electronic effects caused by the electron donation of the silicon to the platinum [19] resulting in a stronger back-donation from the metal to the CO. However, since an exclusively electronic effect should merely increase the absorption intensity [20,21] the observed decrease can be understood only on the basis of a simultaneous dilution of the adsorption sites. The further shift of the HF-band to 2048 cm^{-1} (spectrum D in fig. 1) cannot be explained by geometric effects but must be due to a higher back-donation from the metal to the CO (electronic or ligand effect). The effect of the increase of the $\nu(CO)_b/\nu(CO)_l$ intensity ratio with

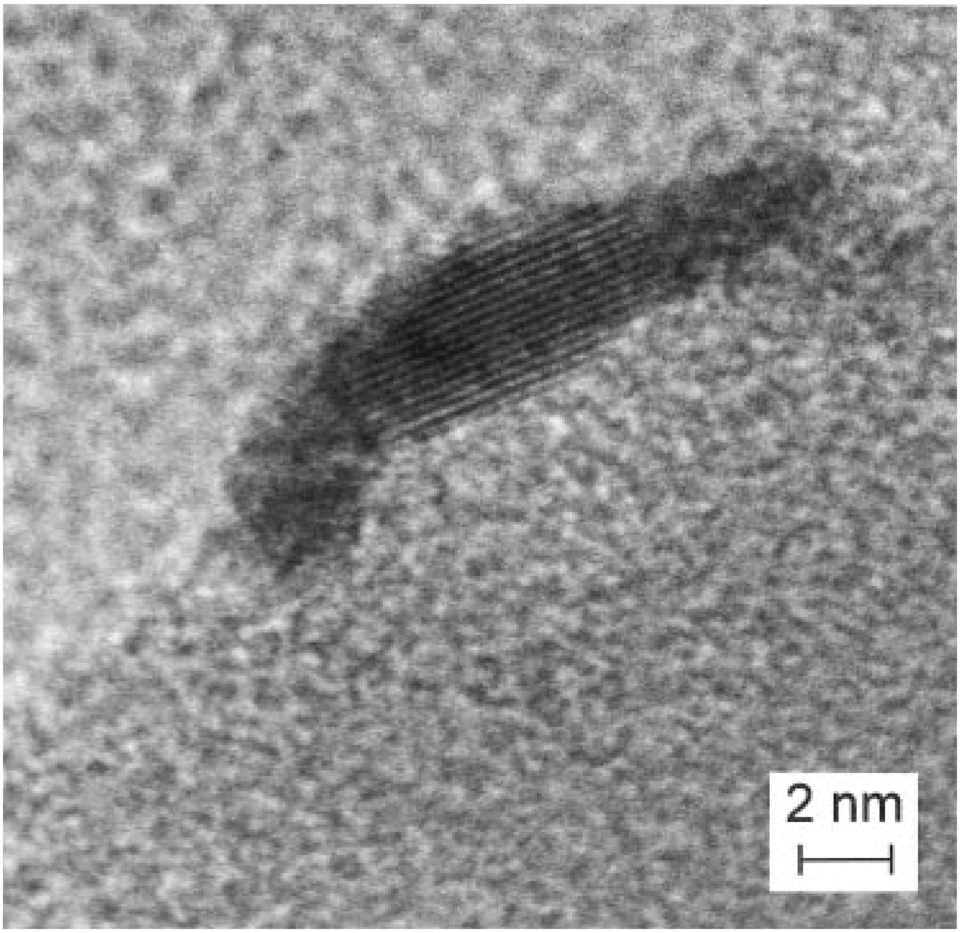

Fig. 3. Electron micrograph of Pt/SiO$_2$ reduced at 923 K.

increasing degree of alloying of the Pt by Si requires further interpretation.

In general, an incorporation of other atoms into a metal lattice results in a contraction of the valence d-bandwidth due to a smaller overlap between the more remote metal atoms [22]. Since chemisorption on a transition-metal surface involves interaction with the s,p- and the d-valence electron band, an influence on the CO chemisorption bond type can be expected from any change of the d-band structure. Considering different symmetries of interaction with the 5σ and $2\pi^*$ orbitals of CO the question whether linear or bridge coordination occurs is the result of a subtle balance between the 5σ (which favours linear) and $2\pi^*$ (which favours bridge coordination) interaction with the d- and s-band of the metal. Van Santen [13] showed that the bridged position becomes more favoured if: (1) the interaction with the d-valence electron bands decreases; (2) electron back-donation from metal to adsorbate becomes more strongly favoured over electron donation from adsorbate to metal; (3) the d-valence electron band significantly depletes, so that interaction of the metal s-band with the 5σ orbital becomes promoted favouring bridge coordination for reasons of local orbital symmetry. Obviously, a full understanding of the chemisorption phenomena requires considerations of global band structures as well as local orbital symmetries. In case of the platinum silicides the smaller d-bandwidth means that the valence d-electron orbitals are less extended and therefore their interaction with CO would be decreased, i.e. the linear-bonded CO should be more disfavoured than the bridge-bonded CO. The observed increase of the $\nu(\mathrm{CO})_\mathrm{b}/\nu(\mathrm{CO})_\mathrm{l}$ intensity ratio might be then a common finding for CO chemisorption on alloys, overrunning the dilution effect, which should lead to a preference of the linearly bonded CO.

After reduction at 923 K a change in particle shape has been observed (fig. 3). The particles, presumably, consisting of Pt$_3$Si in the shell and probably Pt in the core, seem to wet the silica support.

The model of an ‘‘onion-like’’ composition of the alloyed Pt/Si particles is supported by the observation of the 2086 cm^{-1} band shift, starting even at low degrees of alloying.

The missing of a full recovery of the CO band intensity after a cycle of SMSI, i.e. oxidative decomposition of the platinum silicide shell, might be referred to a partial decoration of the metal particles by silica species. The formation of SiO$_2$ layers on top of metal crystals after oxidative decomposition of metal silicides is observed repeatedly, e.g., for Ni_2Si [23] or Pd/Si alloys [24].

5. Conclusions

The high-temperature reduction of a Pt/SiO_2 catalyst prepared via sol–gel processing results in Pt/Si alloys at lower and platinum silicides at higher temperature. From the start of the alloying the $\nu(CO)_l$ band shifts to lower wavenumbers indicating an "onion-like" structure of the alloy.

The decrease of the $\nu(CO)_l$ band intensity at low degrees of alloying demonstrates that the effect of the d-band narrowing overcompensates the ligand effect of Si. This conclusion is supported by the increase of the CO band intensity ratio bridged/linear. The regeneration of the alloys or silicides results in Pt particles decorated by silica species.

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