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Investigations on Silica-Supported Platinum–Silver Alloy Particles by Infrared Spectra of Adsorbed CO and N_2

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The surface properties of specially prepared, silica-supported platinum–silver alloy particles are studied by volumetric chemisorption of H_2, O_2, and NO and infrared spectra of adsorbed CO and N_2. The volumetric experiments show the surface compositions of the alloy particles after reduction and outgassing to be similar to the bulk compositions. Adsorption of CO on reduced pure Pt samples brings about an intense absorption band at 2085 cm^{-1}. For the alloy particles the CO band shifts to 2023 cm^{-1} with increasing silver content, while a weak band at 2164 cm^{-1} is displayed. Mild oxidation (10 Torr O_2) of the alloy particles prior to CO adsorption leads to a drastic decrease of the intensity of the low-frequency band and a simultaneous growth of the high-frequency band, now positioned at 2173 cm^{-1}. As the absorption bands around 2170 cm^{-1} are ascribed to CO bound to Ag^+ ions, these results point to a strong enrichment of the surface with silver due to adsorbed oxygen. Oxidation in 1 atm O_2 at elevated temperatures (300–400°C) causes a redistribution of silver over the alloy particles without a considerable sintering of the entire particles, as can be inferred both from the volumetric and infrared experiments. Infrared spectra of N_2 adsorbed on reduced and thoroughly outgassed samples show the extent of adsorption to drop strongly with increasing silver content of the alloy. This behavior is tentatively ascribed to a strong influence of alloying on the surface structure of platinum particles.

INTRODUCTION

Studying supported monometallic catalysts, we have reported previously on significant changes of the chemisorption properties and the surface structure of the metal particles with the preparation, the pretreatment, and the particle size (*1, 2*). It was concluded that the surface properties of small metal particles are by no means solely determined by the chemical nature of the metal, but are also a function of the history and the chemical environment of the particles. In the case of bimetallic particles matters are even more complicated. Besides the structure, the chemical composition of the surface is now a parameter that has to be considered. The thermodynamic and kinetic properties of the studied alloy ultimately determine the surface composition of the particles. These properties, however, depend on an impressive number of factors, viz. the bulk composition of the alloy, the temperature, the crystal face considered, the particle size, the gas atmosphere, and the interaction with the support (*3–5*).

A complication to be considered when dealing with supported alloy catalysts is the uncertainty about the bulk composition of the particles (*3, 6*). Conventional preparation methods usually lead to catalysts in which the individual alloy particles exhibit a considerable variation in composition. Furthermore, the size of the alloy particles may be a function of their composition. The preparation of the much-studied alloys of a Group VIII and Group IB metal is especially difficult. Impregnation and drying procedures are normally utilized to prepare this type of catalyst. Several papers point

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out, however, that the deposition of a Group VIII and IB metal following these simple procedures, lead to two separate metal phases (*7–10*).

In this work we have investigated PtAg/SiO_2 catalysts prepared with the aim of achieving alloy formation at low temperatures. The bimetallic catalysts were prepared using Pt/SiO_2 as a starting material. Silver was deposited selectively onto the platinum particles by liquid-phase reduction of complex silver ions in an aqueous suspension of the platinum catalyst (*10*). This production method offers two advantages. The variation of the bulk composition of the individual particles is expected to be fairly small after preparation: no silver is deposited separately from platinum particles, while careful work guarantees every Pt particle to be covered with silver. Furthermore, the distribution of platinum metal in the alloy catalysts is identical to that of the original Pt/SiO_2 catalyst. The platinum catalyst used as starting material can be studied in detail. Every difference with the alloy catalysts is solely connected with the addition of silver and not with the particle size or the distribution of the active component over the support.

To study the surface properties of supported alloys, several techniques using selective chemisorption can be usefully applied. Using an adsorbate which interacts mainly with the Group VIII metal, surface compositions of alloys with a IB metal have been estimated from volumetric measurements. Chemisorption-induced surface segregation and changes of the adsorption stoichiometry with alloying hamper the interpretation of the measurements (*11*). Infrared spectra of adsorbed probe molecules shed more light on the surface properties. Supported catalysts of PdAg (*8, 12*), NiCu (*13*), PdAu (*14*), and PtCu (*15*) have been investigated by infrared spectra of adsorbed CO. A drawback of CO adsorption is the risk of surface segregation of the Group VIII metal due to the high heat of adsorption. We therefore amplified the CO adsorption studies with volumetric chemisorption experiments using H_2, NO, and O_2 as the adsorbates. The interaction of Pt with H_2 being more weak than with CO, we expect no interference of chemisorption-induced surface enrichment in platinum at room temperature. Finally, we mention the weak adsorption of infrared-active N_2. Several workers report on the adsorption of N_2 on supported Pt and agree that the coverage of infrared-active species is low (*16, 17*). Van Hardeveld and Van Montfoort (*16*) suggest that the adsorption of N_2 is limited to sites of a special structure on the surface. It is interesting to study the influence of addition of Ag to Pt on the N_2 adsorption to obtain further insight into the surface structure of the alloy particles.

In this paper we report on infrared spectra of CO, NO, and N_2 adsorbed at room temperature on PtAg/SiO_2 catalysts with varying alloy compositions. The measurements were performed after different reducing and oxidizing treatments of the samples. The infrared spectroscopic investigations were supported by volumetric determination of the extent of adsorption of H_2 and NO at room temperature and of O_2 at 170°C. Details about the interaction of NO with Pt/SiO_2 and PtAg/SiO_2 have been published previously (*18*).

EXPERIMENTAL

Silica-supported PtAg catalysts were prepared by homogeneous reduction of $Ag(NH_3)_2^+$ in an aqueous suspension of a 6 wt% Pt/SiO_2 catalyst (Johnson & Matthey, Eurocat). Either formalin or hydrazine was used as reducing agents leading to F- and H-type catalysts, respectively (Table 1). This preparation method assured a very homogeneous distribution of the alloy particles over the support. Electron microscopy revealed that the majority of the alloy particles have sizes in the range 20 to 50 Å. Details of the preparation method and the characterization of the samples have been dealt with before (*10*). It appeared that hydrazine reduction produced some large Ag

TABLE 1

Designations and Atomic Compositions of the Catalysts

Catalyst	At% Ag	At% Pt
Pt/SiO_2	0	100
H9	10	90
F6	31	69
H4	63	37
F2	64	36

particles, whereas formalin selectively deposited Ag onto the Pt particles.

After preparation and drying (120°C) a catalyst was pressed into a self-supporting disk for the infrared transmission measurements. The disk was transferred to an all-glass infrared cell where pretreatment of the sample could be performed *in situ* at temperatures up to 450°C. The cell had been permanently mounted in the sample compartment of a Perkin-Elmer 580B infrared spectrophotometer and coupled to a high vacuum and gas dosing apparatus. Spectra were always recorded at room temperature. Gas phase absorption was compensated for by an identical cell placed in the reference beam of the spectrophotometer. The spectra were corrected for background absorption of the SiO_2 carrier. In studying the adsorption, spectra were measured for CO at a pressure of 100 Torr, for N_2 at 300 Torr, and for NO at 1.0 Torr.

Reduced samples were investigated after keeping the disk at elevated temperatures (usually 400°C) in a flow of 10% H_2/90% Ar overnight. Subsequently the disk was evacuated at the same temperature for 2 hr, which led routinely to a pressure around 5.10^{-7} Torr. Cooling the disk to room temperature did not lead to a significant decrease of the pressure, thereby showing that impurities no longer desorbed from the catalyst surface at 400°C.

For infrared spectroscopic investigations of supported metal catalysts the vacuum conditions in the cell are very critical. Due to the scattering of infrared radiation by the support, thin wafers are necessary to obtain a reasonable signal-to-noise ratio when recording spectra. The necessity of the wafer being thin implies use of a limited amount of a catalyst (about 50 mg). The risk of contamination of the small metal surface thus used is appreciable. Special care was taken to prevent contamination of the metal particles during evacuation after reduction. Besides an oil diffusion pump our vacuum system was equipped with an ion-getter pump (Riber, 25 liters/sec). Adsorption experiments using an adsorbate which covers the metal surface to a large extent were not very sensitive to the vacuum conditions after reduction. On the other hand, the adsorption of molecular nitrogen appeared to depend strongly on the cleaning procedures of the sample. Using the Pt/SiO_2 catalyst we carefully studied the influence of the pretreatment on the absorption band of adsorbed N_2. Starting with a slightly contaminated vacuum system we arrived at a pressure of 1.10^{-6} Torr after evacuation of the freshly reduced sample at 400°C for 2 hr. Subsequent admission of N_2 (300 Torr) did not lead to a detectable infrared absorption band. Prolonged pumping down of the system to the base pressure of 3.10^{-7} Torr, prior to the evacuation of the sample, had a significant influence on the results. Irrespective of the temperature (300–450°C) and time of evacuation (0.5–4 hr) an identical N_2 absorption band was now obtained. At a N_2 pressure of 300 Torr this band was stable for more than 2 hr. These results convincingly demonstrate that, although difficult, it is possible to produce and maintain a clean metal surface in transmission infrared experiments. Other workers have had much difficulty in obtaining stable N_2 absorption bands, owing to the less favorable vacuum conditions (*17*).

Volumetric experiments were performed in a classical Pyrex high vacuum and gas supply system. About 1 g of catalyst was used to record the isotherms. Adsorbed amounts of H_2 and NO were determined at room temperature, while O_2 adsorption was studied at 170°C. The extent of adsorption was evaluated from the isotherms (0–10 Torr) by extrapolating the slowly increasing part to the zero-pressure axis. The pretreatment procedures of the samples were identical to those applied in the infrared experiments.

RESULTS

Chemisorption Measurements

Adsorbed amounts of H_2, NO, and O_2 were determined after reduction and evacuation at 400°C. The results for the fresh catalysts are summarized in Fig. 1. For H_2 and NO the extent of adsorption dropped continuously with the concentration of silver in the alloy. Because of the comparable results with H_2 and NO, we think that these adsorbates do not induce surface segregation of platinum. Furthermore, the relationship between the extent of adsorption and the alloy composition strongly suggests the bulk and surface compositions to be similar. As expected, the interaction of silver with H_2 and NO is weak under these conditions and these adsorbates are appropriate to estimate the number of Pt atoms at the surface. Oxygen, on the other hand, adsorbed both on Ag and Pt as can be inferred from Fig. 1.

After oxidation at 400°C in 1 atm of oxygen and subsequent reduction at that temperature, the extent of adsorption of H_2 and O_2 was redetermined. In Fig. 2 the ratio of the adsorbed amounts before and after oxidation has been plotted against the alloy composition. For Pt/SiO_2 neither the H_2 nor the O_2 adsorption had decreased. With increasing silver content of the alloy the O_2 uptake decreased slightly, whereas the H_2 adsorption dropped to a much larger extent. Roughly speaking, the extent of O_2 adsorption is proportional to the total metal surface area and that of H_2 adsorption to the platinum surface area. The results of Fig. 2 therefore suggest that oxidation at 400°C leads to a redistribution of the silver phase over the alloy particles without any considerable mobility of platinum.

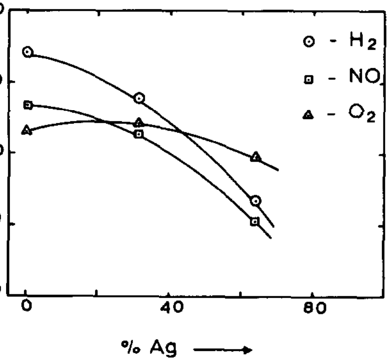

FIG. 1. Adsorbed amounts of H_2 and NO at room temperature and O_2 at 170°C as a function of alloy composition.

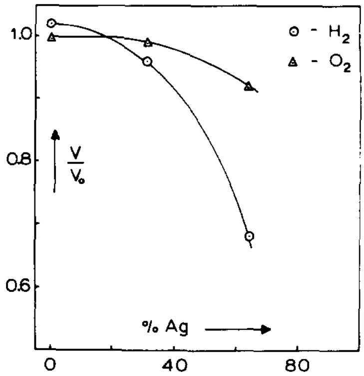

FIG. 2. Adsorbed amounts of H_2 and O_2 on the catalysts after oxidation and subsequent reduction at 400°C. The extent of adsorption (V) has been divided by that prior to oxidation (V_0).

Infrared Spectra of Adsorbed CO

The investigations were started with catalyst F2, which contained 64 at% silver, to establish the influence of the pretreatment. Figure 3 shows infrared spectra of CO adsorbed on the catalyst which had been reduced before and after an oxidation treatment at 300°C in 1 atm of O_2 for 16 hr. Due to the oxidation treatment the main absorption band shifted to lower frequencies while its intensity dropped. Before oxidation a shoulder around 2070 cm^{-1} was observed which had disappeared afterward. Moreover, the previously oxidized catalyst dis-

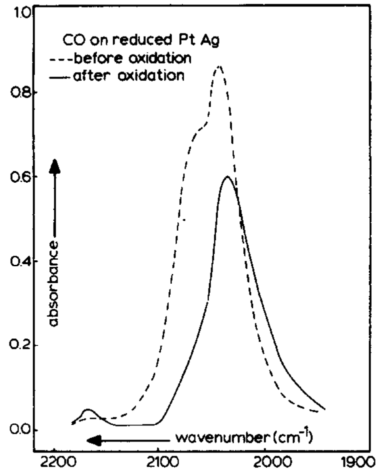

FIG. 3. Infrared spectra of CO adsorbed on PtAg/ SiO_2 catalyst F2 (64 at% Ag), which had been previously reduced. The reduction was performed before and after an oxidation treatment at 300°C.

played a weak band at 2165 cm^{-1}. Pumping off the gaseous CO brought about the disappearance of the 2165 cm^{-1} band, whereas the main peak remained virtually unchanged. Prolonged reduction at 400°C shifted the main peak further, from 2035 to 2023 cm^{-1}, but without a change of the intensity. Prior to the experiments to be described below, the sample had always been treated in 1 atm of oxygen at 300 or 400°C.

Bimetallic catalysts of a different composition were next studied, after reduction at 400°C. The infrared spectra of CO adsorbed on catalysts F2 and F6 together with that on Pt/SiO_2 are shown in Fig. 4. The very intense band displayed by Pt/SiO_2 peaked at 2085 cm^{-1}. A considerable coincidence of the bands from F6 and Pt/SiO_2 was observed, whereas the band of F2 was situated at rather lower frequency. From Fig. 4 it can be concluded with certainty that the main band displayed by the alloys is due to CO bound linearly to Pt atoms at the surface. Apparently, alloying of Pt with Ag shifts the vibrational frequency of adsorbed CO to lower values as will be discussed in more detail below. The absence of the 2165 cm^{-1} band with Pt/SiO_2 is another remarkable feature of Fig. 4. The absence on pure platinum suggests the high-frequency band to be connected with CO on silver sites. The same frequency has indeed been observed for CO adsorption on silver (*2*). The band was ascribed to CO bound to Ag^+ ions. This assignment implies that the alloy particles contain some Ag^+ ions, and thus residual oxygen, even after reduction at 400°C.

During CO adsorption on reduced alloy particles we observed a slow increase of the absorption band with the time of exposure. The increase was larger than could be explained by a slow transport of the adsorbate through the narrow pores of the support. The increase could mount up to 30% of the intensity measured immediately after dosing of the CO, while a small shift of the band maximum to higher frequencies was simultaneously observed (typically 4 cm^{-1}). We have to conclude that the CO molecules do bring about a significant enrichment in platinum of the surface. Infrared spectra of adsorbed CO on reduced alloy particles are therefore not suitable for quantitative determination of the surface composition. Because the frequency of the absorption bands did not shift considerably with time we believe, however, that the position of

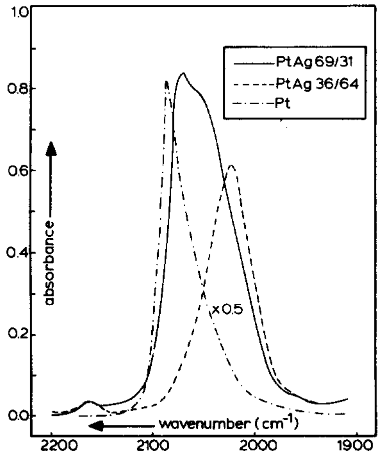

FIG. 4. Infrared spectra of CO adsorbed on reduced catalysts; Pt/SiO_2 and $PtAg/SiO_2$ catalysts F2 (PtAg 36/64) and F6 (PtAg 69/31). Note that the intensity of the Pt/SiO_2 spectrum has been reduced by a factor of 2.

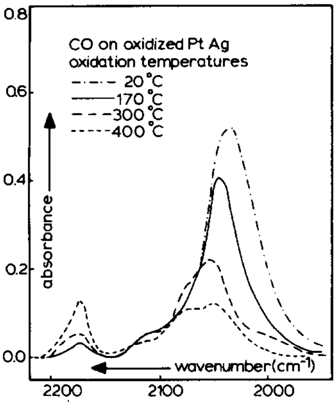

FIG. 5. Infrared spectra of CO adsorbed on PtAg/SiO_2 catalyst F2 (64 at% Ag) after oxidation with 10 Torr O_2 at different temperatures.

the bands gives qualitative information on the condition of the surface.

To establish the influence of adsorbed oxygen on the alloy particles, catalyst F2 was exposed to 10 Torr O_2 at different temperatures. After evacuation at the same temperature for 30 min, the sample was cooled to room temperature and CO was adsorbed. The results are summarized in Fig. 5. With increasing oxidation temperature the main absorption band, situated around 2050 cm^{-1}, shifted to higher frequencies whilst its intensity dropped. The weak band, ascribed to CO bound to Ag^+ ions, was now positioned at 2173 cm^{-1}. The intensity of this band increased with the oxidation temperature. The results suggest that oxygen sorption induces enrichment of the surface in silver. This will be understood more readily when we consider the next experiments.

Catalysts F2 and F6 were studied together with Pt/SiO_2 after oxidation at 400°C in 10 Torr O_2. CO adsorption on the thus oxidized samples produced the spectra of Fig. 6. Several important features should be noted when comparing the results with CO adsorption on the reduced samples (Fig. 4). Pure platinum displayed a band with the maximum at 2090 cm^{-1} while the reduced sample exhibited the maximum at 2085 cm^{-1}; the intensity is almost identical for reduced and oxidized platinum. In line with Heyne and Tompkins (*19*) we conclude that the large similarity of the CO adsorption on reduced and mildly oxidized platinum is due to a fast reduction of the metal particles by CO. After removal of adsorbed oxygen as CO_2 the thus cleaned surface adsorbs CO as does a hydrogen-reduced bare platinum surface. With alloy particles, on the other hand, a drastic change of the infrared band upon oxidation was observed (compare Fig. 3 with Figs. 5 and 6). We note that CO at room temperature is not able to reduce the alloy surface to a large extent. Apparently, the reducibility of PtAg has been lowered if compared with Pt. An important conclusion is that the spectra of CO adsorbed on mildly oxidized samples give a fair estimation of the degree of coverage of the platinum particles with silver. This was used elsewhere to evaluate the preparation procedure of the alloy catalysts (*10*).

Besides the oxidation temperature, the oxygen pressure appeared to be an important parameter controlling the extent of oxidation of the alloy particles. Figure 7 reveals infrared spectra after oxidation of catalyst F2 at 300°C in both 10 and 760 Torr O_2. The higher oxygen pressure brought about a band at 2100 cm^{-1} and a still further

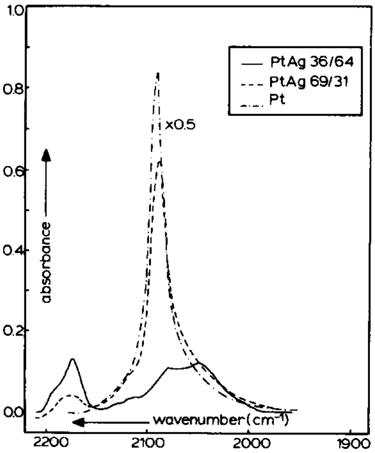

FIG. 6. Infrared spectra of CO adsorbed on the oxidized catalysts (400°C, 10 Torr O_2). Catalyst F2 (—), F6 (---), and Pt/SiO_2 (–·–·–).

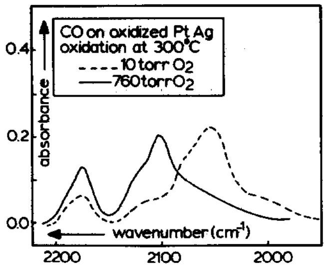

FIG. 7. Infrared spectra of CO adsorbed on PtAg/SiO_2 catalyst F2 (64 at% Ag) after different oxidation treatments.

TABLE 2

Frequencies and Intensities at the Band Maxima of Adsorbed N_2 (300 Torr) on Reduced Platinum Bimetallic Catalysts

Catalyst	At% Ag	$\nu(N_2)$, cm^{-1}	Absorbance
Pt/SiO_2	0	2230	0.132
H9	10	2227	0.083
F6	31	2214	0.024
H4	63	2210	0.008

increase of the 2173 cm^{-1} band. Following Heyne and Tompkins (*19*) we attribute the 2100 cm^{-1} band to CO bound to Pt^{2+} ions. Obviously, oxygen atoms penetrate into the alloy particles at high pressures and are strongly held. CO is no longer able to reduce the platinum sites present in the alloy surface and adsorbs on the oxidized atoms. Comparing Figs. 5 and 7, the O_2 pressure seems to be more important than the oxidation temperature in controlling the extent of subsurface oxidation of the alloy particles.

Infrared Spectra of Adsorbed N_2

Nitrogen adsorption was investigated on the catalysts after reduction and thorough outgassing at 400°C. The infrared spectra of adsorbed N_2 appeared to be pressure dependent. To obtain measurable intensities the absorption bands were recorded at a N_2 pressure of 300 Torr. Table 2 summarizes the frequencies and intensities of the band maxima for the catalysts investigated. With increasing silver content of the alloy catalysts both a lowering of the frequency and a strong decrease of the intensity was observed. To obtain more insight into the influence of alloying on the N_2 adsorption, we have plotted the intensity as a fraction of the absorbance on pure Pt against the composition of the alloy (Fig. 8). For comparison the integrated intensities of the absorption band of adsorbed NO (1 Torr, room temperature) on the same catalysts have been added. The intensity of adsorbed NO fell linearly with increasing silver content, whereas N_2 adsorption decreased much more steeply. In accordance with the volumetric experiments, the results indicate the number of adsorbed NO molecules to be simply proportional to the number of Pt atoms in the alloy surface. The adsorption of infrared-active nitrogen is influenced more drastically by alloying. The reason for this will be discussed in more detail below.

DISCUSSION

Infrared Spectra of Adsorbed CO

The vibrational frequency of adsorbed CO is sensitive to the amount of silver in the bimetallic catalysts. Concerning the re-

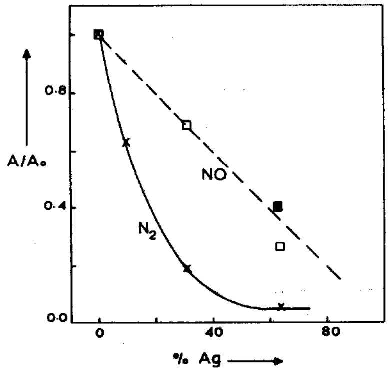

FIG. 8. Intensities of infrared absorption bands (*A*) plotted as a fraction of the intensity measured for pure platinum (A_0) against the alloy composition. For NO the integrated band intensities have been used for N_2 the absorbance at the peak frequency.

duced samples, the absorption band shifts from 2085 cm^{-1} for pure platinum to 2023 cm^{-1} for catalyst F2 containing 64 at% of silver (Fig. 4). In spite of this considerable shift, we believe that with all samples the main band must be ascribed to CO linearly bound to Pt sites. Dilution of the Pt sites with Ag brings about the shift to lower frequencies. The explanation for the shift due to alloying concerns both electronic and geometric factors. A discussion of the relative importance of these factors has been put forward by Toolenaar *et al.* (*15*, *20*) and will not be repeated here. Concerning the PtAg system, we think that a decrease of the dipole–dipole coupling due to a larger mutual distance between the vibrating CO molecules can account for the greater part for the frequency shift (*21*).

The small, strongly pressure-dependent band around 2170 cm^{-1} is absent with Pt/SiO_2. The appearance of this band with the alloy catalysts suggests it to be connected with the presence of silver. In previous work on CO adsorption on Ag/SiO_2 catalysts a band at 2173 cm^{-1} was found with oxidized samples, while reduced catalysts displayed a band at 2164 cm^{-1} (*2*). It is noteworthy that these frequencies match exactly with the frequencies for oxidized and reduced alloy particles, respectively. With Ag/SiO_2 catalysts the absorption bands were invariably attributed to CO bound to Ag^+ ions. Because of the exact coincidence it is tempting to ascribe the bands around 2170 cm^{-1} to Ag^+ ions also with the alloy catalysts. This assignment implies the presence of oxygen in the alloy particles, even after reduction at 400°C. The results of Fig. 3 show that the oxidation treatment induces the appearance of the 2170 cm^{-1} band. We think that during oxidation in 1 atm O_2 considerable penetration of oxygen atoms into the alloy particles proceeds (see also Fig. 7). The subsequent hydrogen reduction is not sufficient to remove all of the subsurface oxygen. The oxygen remaining after reduction ultimately causes the appearance of the 2164 cm^{-1} band. Strong retention of subsurface oxygen has also been observed with silver catalysts (*2*).

Oxidation of the alloy catalysts in 1 atm of oxygen in the temperature range 300–400°C brings about a redistribution of silver without appreciable sintering of the alloy particles. This can be inferred from the chemisorption results of Fig. 2 and the shift of the CO absorption bands to lower frequencies upon oxidation (Fig. 3). Moreover, pure platinum is not sensitive to the oxidation treatment (Fig. 2). Redispersion of a metal in an oxidizing environment has often been ascribed to wetting of the support by the metal oxide (*22*). This mechanism would imply, however, that phase segregation occurs between platinum and silver after subsequent reduction, which is not observed in our work. Phase segregation due to oxidation has been found and described by De Jongste and Ponec (*23*) for platinum–gold on alumina. Furthermore, silver oxide is not stable under the experimental conditions applied. We prefer, therefore, a description visualizing mobile, oxygen-containing silver clusters. These clusters dissociate from silver-rich alloy particles and are captured by particles which contain less silver.

The chemisorption results obtained with H_2 and NO (Fig. 1) do not provide evidence for surface enrichment in either of the components for the PtAg particles after reduction and outgassing at 400°C. This is confirmed by the infrared spectra of adsorbed CO. The integrated intensities of the absorption bands reproduced in Fig. 4 even suggest surface segregation of platinum. Unfortunately, CO adsorption is not suitable for estimating the surface composition: the time dependence of our spectra suggests that CO induces enrichment of the surface in platinum. None of the results obtained by us point to surface segregation of silver after reduction and evacuation of the PtAg particles. Simple theories for alloys, based on the broken-bond model, would predict a strong surface enrichment in silver due to its low heat of atomization (*11, 24*). In line with work on PdAu particles of about 30 Å (*14, 25*) our results suggest that bulk thermodynamics are not appropriate to describe the behavior of the very small (alloy) particles.

The results of Figs. 5–7 show that oxygen adsorption on the alloy particles brings about a considerable enrichment in silver of their surfaces. Whereas a platinum surface is easily reduced by CO at room temperature, the reducibility of the alloy surfaces drops steeply with their silver content (Fig. 6). With increasing oxidation temperature the number of Ag^+ ions increases and the amount of reducible platinum surface decreases (Fig. 5). As discussed above, the absorption band around 2050 cm^{-1} is ascribed to reduced Pt sites while CO bound to Pt^{2+} ions is thought to cause a band at 2100 cm^{-1}. This assignment implies that oxidation of $PtAg/SiO_2$ by exposure to 10 Torr O_2 at different temperatures (Fig. 5) mainly leads to superficial oxidation and enrichment in silver of the surface. Oxidation in 1 atm of O_2 (Fig. 7) also leads to penetration of oxygen and an amount of Pt^{2+} ions not reducible at room temperature.

Chemisorption-induced surface segregation has been reported by several authors. Williams and Boudart (*26*) found a surface enrichment in gold in their AES study of NiAu foils. Oxygen adsorption caused the Au atoms to vanish from the surface. This was attributed to surface segregation of Ni atoms, since the Ni–O bond is stronger than the Au–O bond. Similar observations were made for the Pd–Ag (*27*) and Pt–Sn (*28*) systems. In these cases CO adsorption caused segregation of the Group VIII metal at the surface. The enrichment in silver of the PtAg surface upon adsorption of oxygen is not trivial. Considering both the thermodynamic stabilities of the oxides (*29*) and the heats of adsorption of O_2 on the metals (*30*), one would expect an enrichment in platinum. A higher affinity of the silica support for Pt ions than for Ag ions (*31*) may play an important role when considering the oxidation behaviour of the very small PtAg particles.

Infrared Spectra of Adsorbed N_2

The adsorption of infrared-active N_2 species on metal surfaces has been a matter of considerable discussion in the literature (*16–18*). Van Hardeveld and Van Montfoort (*16*) have described the adsorption as a physical interaction of N_2 with sites on the metal surface of a certain geometrical configuration (so-called B_5 sites). Other workers prefer description as a weak chemisorption (*17*). Although the description of the N_2 adsorption is not essential to our work, we slightly prefer the physical model because the infrared frequency is relatively insensitive to the chemical nature of the adsorbing metal (*17*). However, an important conclusion from the literature is that the adsorption of infrared-active N_2 is restricted to low coverages and concerns special sites on the surface. As discussed above, the vacuum conditions are critical when studying N_2 adsorption with supported metal catalysts, which points to a high sensitivity of the special sites for poisoning by, e.g., oxygen and hydrocarbons.

With increasing silver content of the alloys, the adsorption of infrared-active nitrogen fell steeply (Fig. 8). This observation can be explained in several ways. The possibility exists that N_2 adsorbs exclusively on ensembles of several platinum atoms in the alloy surface. Assuming a random mixing of atoms in the surface, the number of large ensembles of platinum atoms falls strongly with increasing silver content. This ensemble-size effect would readily explain the phenomena observed. Although we cannot rule out this possibility, there are reasons to believe that N_2 adsorbs on sites of a certain geometry, irrespective of the nature of the metal atoms. Adsorption on ensembles consisting of both elements accounts for the frequency shift of N_2 with the alloy composition (Table 2). We tentatively ascribe the suppressing of the adsorption by alloying to a decrease of the number of sites structurally suited for binding N_2. One can consider it as a smoothing of the platinum surface by silver atoms which fill up the sites able to bind nitrogen in an infrared-active state. This reasoning is in accordance with Sundquist's work (*32*) which demonstrates a drastic influence of alloying on the surface structure of metals.

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