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PRODUCTION OF SUPPORTED SILVER CATALYSTS BY LIQUID-PHASE REDUCTION

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ABSTRACT

Supported silver catalysts are prepared by reduction of complex silver ions by a suitable reducing agent in an aqueous suspension of the carrier. Ammonia or EDTA are used as ligands for the silver ions. Favourable preparation conditions to enhance the silver dispersion appear to be homogeneous addition of the reducing agent, a strong interaction between the silver complex and the support, and the absence of micropores in the carrier.

Ag/SiO_2 catalysts prepared by reduction of $Ag(NH_3)_2^+$ with formalin typically display a bimodal particle-size distribution. Particles nucleated on the support have sizes of 35-70 Å, whereas particles formed in the liquid phase are considerably larger (200-400 Å). A more or less fundamental lower limit of the average particle size for the silver-silica system of about 60 Å has been recognized and explained in terms of the high mobility of silver particles over silica surfaces.

INTRODUCTION

Supported monometallic catalysts are usually prepared by impregnation of the support with a solution of the metal salt followed by evaporation of the solvent. Provided the support does not adsorb the active ions or atoms to a considerable extent, the precursor of the active component is uniformly distributed in the pore volume of the carrier. In the case of strong (monolayer) adsorption of the active component by the support, impregnation leads also to a good distribution, although it may not be uniform throughout the porous particles or bodies of the support. Several workers [1-3] agree that it is the drying step which gives rise to a significantly inhomogeneous distribution of the active precursor. Improvements of the drying step, such as a high drying rate [2], a high viscosity of the solution [3] and the use of non-aqueous solvents [4], have been proposed. During the preparation of catalysts the drying step can be circumvented, however, by a reactive precipitation of

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the active precursor. Both Van Dillen et al. [1] and Anderson [5] conclude that the metal dispersion will usually be improved if the solid is deposited from the solution by precipitation due to chemical reaction rather than by solvent evaporation.

Previous work from our laboratory has concentrated on precipitation of the active precursor by changing the pH of the solution [1,6,7]. The importance of a homogeneous solution during precipitation and the interaction of the precursor of the active component with the carrier have been dealt with in the previous publications. Because there are cases where deposition-precipitation by changing the pH is not suitable, we report an alternative method involving a change of the valency of the metal ions [8]. We will make use of the differences in the solubility of atoms merely displaying a varying valency.

This paper is devoted to the preparation of silica- and alumina-supported silver catalysts by liquid-phase reduction of complex silver ions in an aqueous suspension of the support. We want to establish the factors which control the dispersion and the distribution of metallic silver on the support. To that end several preparative conditions are varied, viz. the reducing agent, the temperature of the suspension, the concentration of reagents and the complexing agent. After preparation the catalysts are characterized by electron microscopy, oxygen chemisorption and X-ray diffraction.

EXPERIMENTAL

Silver catalysts were prepared by reduction of complex silver ions by a suitable reducing agent in an aqueous suspension of the carrier. Ammonia* or the disodium salt of ethylenediaminetetraaceticacid (EDTA) were used to form silver complexes. The reduction was performed with formaldehyde or hydrazine. Unless stated otherwise, the reducing agent was added by injection of a solution into the suspension through a capillary tube having its end below the level of the liquid. During injection the suspension was vigorously agitated. The liquid-phase reduction was continued for two hours. The temperature of the suspension was varied between 20 and 50°C. The carriers used were non-microporous silica (Degussa BRD, Aerosil 200V and 380V) and microporous γ-alumina (Harshaw, Al-1401P, BET surface area 176 m^2/g).

Because under the experimental conditions mentioned oxygen is able to re-oxidize metallic silver deposited on the carrier, air was excluded during the liquid-phase reduction by working in an N_2 atmosphere. The concentration of silver ions in the solution during precipitation was continuously measured by

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* In the absence of stirring, silver-ammonia solutions spontaneously form extremely explosive silver-nitrogen compounds.

means of a combination of a silver-ion selective electrode (Philips IS 550-Ag^+) and a reference electrode (Philips R44/2-SD/1).

Characterization of the samples dried at 120°C by X-ray diffraction was done using a Debije-Scherrer camera. Determination of the surface area of the supports using N_2 as an adsorbate at 78 K was performed with a Carlo Erba Sorptomatic. Using a classical Pyrex high vacuum and gas dosing system silver surfaces were measured by adsorption of O_2 at 170°C (O_2 pressure 7 Torr, adsorption time 2 hr). Provided no impurities are present in the silver particles, this procedure leads to a monolayer of adsorbed oxygen atoms [9-11]. To calculate the silver surface from the extent of adsorption we assumed an amount of 0.27 ml(STP)O_2/m^2 Ag [10]. With Ag/SiO_2 catalyst 50-F-10 we calculated the silver surface area both from oxygen chemisorption and from a particle-size distribution determined by electron microscopy. The surface areas thus calculated agreed within the experimental error.

The catalysts were examined in great detail by electron microscopy. For scanning electron microscopy a Cambridge 150S microscope was used. This microscope has been equipped with an X-ray analysis (EDS) and a backscattered electron image (BEI) option. Transmission electron microscopy was done using both a Philips EM301 and a Jeol 200C microscope.

RESULTS AND DISCUSSION

Preliminary studies

Preparing silica-supported silver catalysts by reduction of Ag^+ ions without using a complexing agent inevitably led to very large Ag crystallites which did not adhere to the support. This unfavourable result can be ascribed to two simultaneously acting factors: First of all the concentration of 'free' silver ions was high and secondly the interaction between positive ions and SiO_2 particles is weak at pH-levels below about 7 [12]. These factors promote the formation of (large) silver particles in the liquid phase. Both to decrease the effective concentration of silver ions and to control the silver-support interaction, complex silver ions were used in subsequent experiments.

Ammonia and EDTA were used as complexing agents. According to thermodynamic data Ag-NH_3 and Ag-EDTA complexes have almost the same stability [13]. Consequently, the reduction potential of both silver complexes will be the same. It was therefore surprising that in the presence of SiO_2 formalin was able to reduce $Ag(NH_3)_2^+$ at room temperature, whereas higher temperatures were required to reduce the Ag-EDTA complex. The difference in the reduction rate of the complexes revealed the catalytic function of the support for the formation of silver particles. A considerable interaction between the support and the complex silver ions appears to be a prerequisite for smooth nucleation of the metal particles on the support. Working amply above the isoelectric

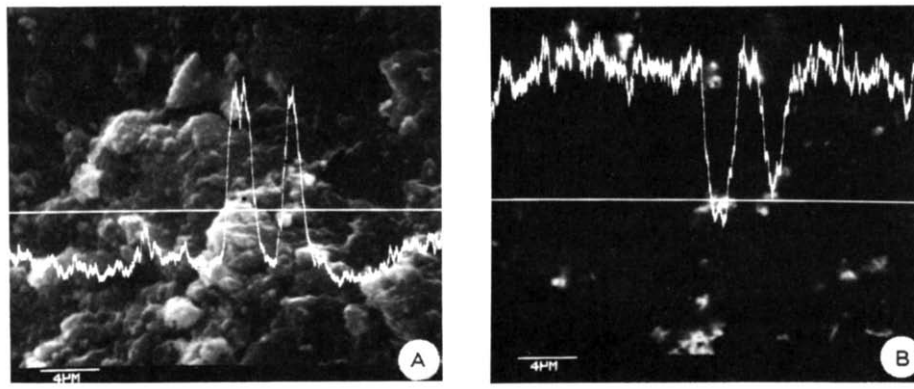

FIGURE 1 Scanning electron micrographs of 10 wt.% Ag/SiO_2 catalyst prepared by hydrazine reduction of Ag-EDTA. (A) Secondary electron image with Ag line scan. (B) Backscattered electron image with Si line scan of the same part of the sample.

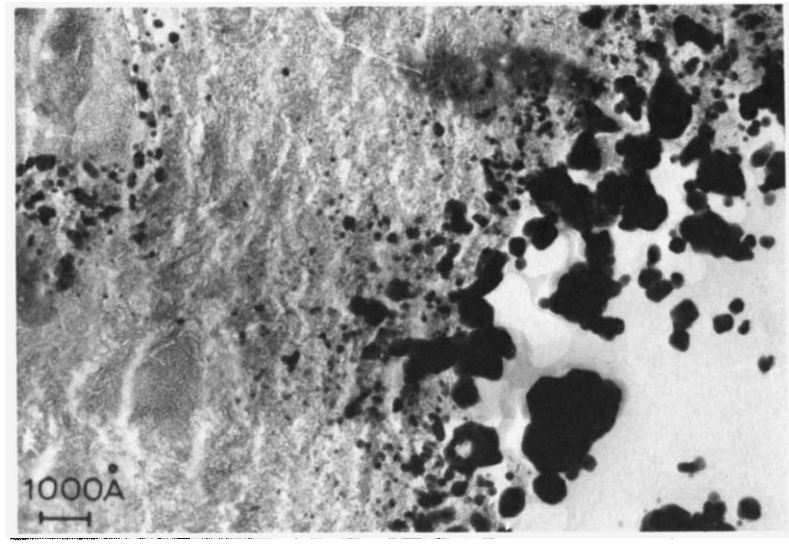

FIGURE 2 Transmission electron micrograph of 25 wt.% Ag/Al_2O_3 catalyst prepared by reduction of Ag-EDTA by hydrazine.

point (IEP) of SiO_2 (about pH=2), the silica particles are negatively charged and mainly interact with surrounding cations. The negatively charged Ag-EDTA complex does not exhibit this interaction and formation of metal particles is inhibited. Brunelle [12] arrived at similar conclusions for the preparation of supported catalysts by metallic complex adsorption.

At 25°C a stronger reducing agent, viz. hydrazine, was used to reduce the Ag-EDTA complex in a suspension of the SiO_2 carrier. A typical example of a catalyst produced by hydrazine reduction was investigated by elemental analysis in the scanning electron microscope. This investigation revealed large clustered silver particles which did not adhere to the support (fig.1). Transmission electron micrographs of Ag/SiO_2 catalysts prepared by reduction of the Ag-EDTA complex showed besides the very large particles detected by SEM, a minimum particle size of about 400 Å (see also fig. 3B). With EDTA as a complexing agent reduction of silver ions does not lead to a homogeneous distribution of the metal over the SiO_2 support, while particles smaller than 400 Å are hardly observed.

Continuing our efforts with the microporous γ-Al_2O_3, we reduced the Ag-EDTA complex with N_2H_4 solution at room temperature. Working below the IEP of alumina (pH 6 to 9), the support particles are now positively charged. Here we met another problem, however, to produce catalysts by liquid-phase reduction viz. the microporosity of the carrier. A typical example of an Ag/Al_2O_3 catalyst has been reproduced in fig.2. Large, clustered silver particles at the edge of the support can be seen together with small silver particles, the number of which decreases steadily with the penetration depth into the support. It seems to us that the absence of silver particles in the small pores of the support is due to the fact that prior to reduction silver ions did not penetrate into the pores. Harriot [14] made similar observations and concluded that a non-microporous support is to be preferred in the production of supported silver catalysts. Apparently, with a microporous support the large internal surface area cannot be used effectively and large silver particles are formed at the (small) external surface of the carrier.

We want to emphasize another feature of the Ag/Al_2O_3 catalysts as e.g. reproduced in fig.2. Detailed examination of the micrographs revealed that the minimum size of the silver particles is now well below 100 Å. The low minimum particle size reflects the interaction between the Ag-EDTA complex and the Al_2O_3 surface to be enhanced if compared with SiO_2.

Preparative variables for Ag/SiO_2

We now turn to the reduction method which produced the highest dispersion of silver particles on SiO_2. This method has been investigated most thoroughly. We produced the Ag/SiO_2 catalysts by suspending the silica in an aqueous

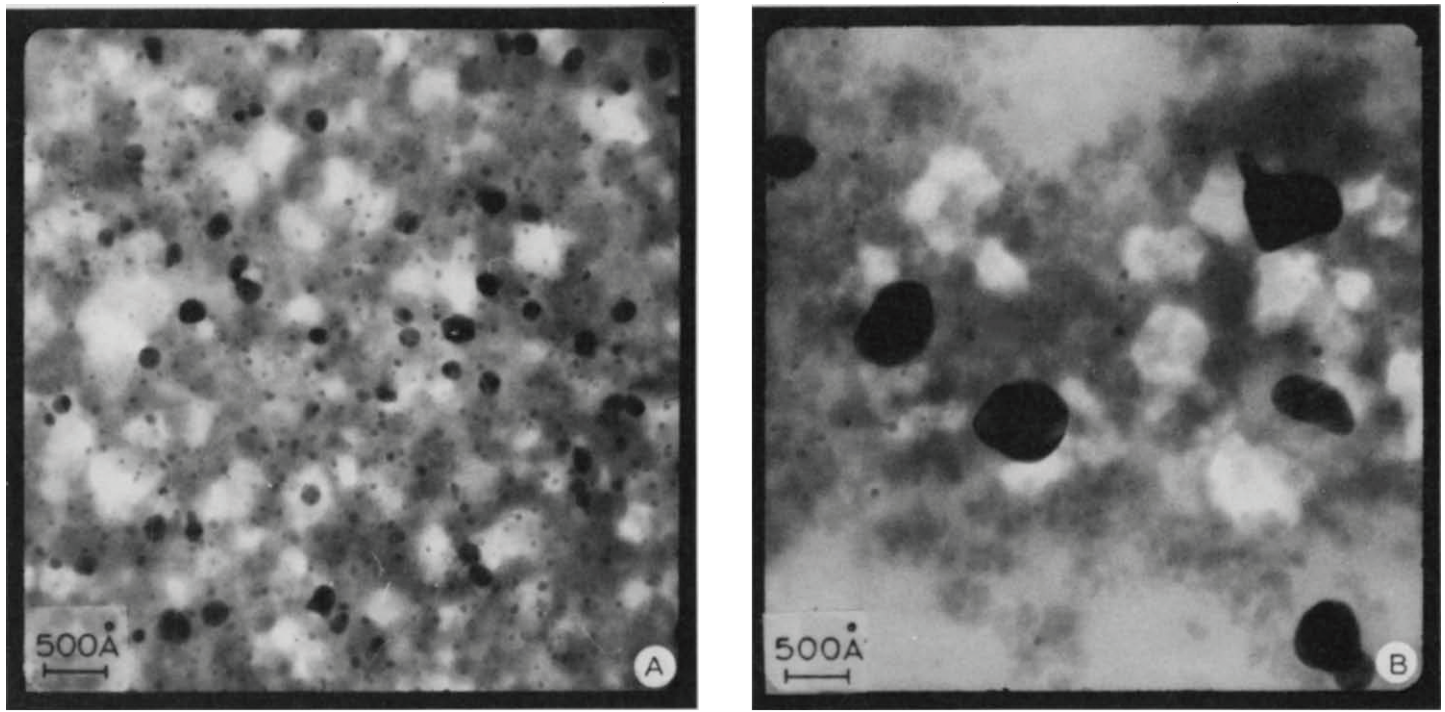

FIGURE 3 Transmission electron micrographs of Ag/SiO_2 catalysts. (A) Sample 50-F-10 produced by formalin reduction of $Ag(NH_3)_2^+$. (B) Sample produced by formalin reduction of Ag-EDTA complex at 60°C.

solution of $Ag(NH_3)_2^+$ and carrying out the reduction with formalin. The parameters varied were the surface area of the support, the temperature of the suspension, the initial concentration of dissolved silver and the way formalin was added. The catalysts are designated by a code like 50-F-10 where 50 refers to the temperature of the suspension during reduction (50°C) and 10 denotes the loading of silver in wt.%. After washing and drying the catalysts were investigated by X-ray diffraction, transmission electron microscopy and oxygen chemisorption. Table 1 gives a survey of the catalysts, the preparation parameters and the specific silver surface areas calculated from oxygen chemisorption. Figure 3A shows an electron micrograph demonstrating the bimodal particle-size distribution typical for this type of catalysts. The small particles are around 50 Å, while the large particles are in the range 200-400 Å. From this broad particle-size distribution it has to be expected that X-ray diffraction line-broadening, producing a volume-average particle size, is not very useful for studying these catalysts. Indeed, the X-ray diffraction pattern exhibited a metallic silver pattern of fairly sharp maxima.

Parameters of the preparation promoting a high silver surface area of the resulting Ag/SiO_2 catalysts can be deduced from table 1. A high surface area of the support, a low silver concentration of the initial solution, and homogeneous addition of the reducing agent are favourable parameters. The influence of the temperature of the reduction is less unequivocal and will be discussed below. From the favourable parameters together with the catalytic function of the support for the reduction of the silver complex, we postulate that the formation of Ag particles is controlled by a rate-determining nucleation and growth process. We think that the large particles (~300 Å) have nucleated in the liquid phase, while the small particles (~50 Å) have been formed from silver ions adsorbed on the support. The differences in silver surface area of the catalysts prepared, now can be translated (oversimplifiedly) as a shifting of the ratio of the number of particles nucleated in the bulk solution and on the surface of the carrier. At this point we want to emphasize that the formation of the 50 Å particles is closely connected with the interaction between the positively charged $Ag(NH_3)_2^+$ complex and the negatively charged SiO_2 particles. In the absence of this interaction as between the negatively charged Ag-EDTA complex and SiO_2, the large Ag particles nucleated in the liquid phase are predominantly formed (fig. 3B).

We will now explain the influence of the preparation conditions on the catalyst dispersion. The rate of addition of formalin has a small but significant influence on the silver particle-size distribution (compare e.g. catalysts 50-F-15/1 and 50-F-15/2). Fast addition leads to a high local concentration of the reactants where formalin enters the suspension. Before the formalin can diffuse into the pores of the suspended support, it will

TABLE 1

Ag/SiO_2 catalysts prepared by liquid-phase reduction as described in the text. T is the temperature of the suspension during reduction. Formalin addition by injection (a); addition of the total amount of formalin at once at temperature T (b); formalin added at 5°C, whereafter the suspension was heated to the temperature T (c). S_{Ag} is the specific silver surface area deduced from oxygen chemisorption.

Catalyst	SiO_2 (m^2/g)	$[Ag(NH_3)_2^+]$ (mmol/l)	T (°C)	Formalin addition	Loading (wt.%)	S_{Ag} ($m^2Ag/g\ Ag$)
50-F-10	380	5	50	c	10	23
20-F-16	380	50	20	c	16	19
20-F-15/1	200	50	20	a	15	5.4
20-F-15/2	200	10	20	a	15	9.7
20-F-15/3	200	10	20	b	15	8.9
20-F-15/4	200	10	20	c	15	11.5
50-F-15/1	200	10	50	a	15	7.1
50-F-15/2	200	10	50	b	15	6.6
50-I-15*	200	--	50	-	15	4.4**

* Catalyst prepared by impregnation of the support with an $AgNO_3$ solution followed by drying at 50°C.

** Estimated from oxygen chemisorption at 170°C. The value is not accurate because of interference of bulk oxidation of the silver particles [11].

produce large silver particles in the liquid phase.

Comparison of the catalysts 20-F-15/1 and 20-F-15/2 (table 1) shows a change in the silver surface area of almost a factor of two due to a difference of the initial concentration of $Ag(NH_3)_2^+$. A high silver concentration will promote the nucleation process both in solution and on the support. Apparently, the nucleation process in the liquid phase is affected most strongly, while the formation of Ag particles on the support is governed largely by the interaction between the silver complex and the support, the latter being independent of concentration.

From catalyst 20-F-16 and 20-F-15/1 (table 1) it can be inferred that a large surface area of the support raises the number of small particles nucleated on the carrier. Assuming a limited and constant number of nuclei on the support per unit surface area, this can readily be understood.

The influence of the temperature of the suspension during reduction (T in table 1) is less straightforward. Comparing catalysts 20-F-15/2 and 50-F-15/1 indicates a negative influence of a high reduction temperature. Clearly, addition of formalin at 50°C leads to more rapid nucleation in the liquid phase than does addition at 20°C. On the other hand, addition at a low temperature where no reaction proceeds, viz. 5°C, followed by heating led to a large number of small silver particles (e.g. catalyst 50-F-10). Addition at low temperature gives a homogeneous solution prior to reduction. Heating of the homogeneous solution to a high reduction temperature promotes nucleation both in the liquid phase and on the carrier thereby enhancing the silver surface area (compare catalysts 50-F-10 and 20-F-16).

The size of the silver particles

Having explained the influence of the preparation conditions on the silver dispersion qualitatively, we turn to the absolute value of the size of the silver particles. From a particle size distribution obtained from an electron micrograph of catalyst 50-F-10 (fig. 3A) it followed that particles having diameters between 35 and 70 Å are most numerous. This is in quantitative agreement with other workers producing small Ag particles on silica. Jarjoui et al [15] prepared an Ag/SiO_2 catalyst by ion-exchange of the support with $Ag(NH_3)_2^+$ followed by reduction in H_2 at 250°C. They observed a maximum in the silver particle size distribution at 40-80 Å. Producing Ag particles on Vycor glass by the incipient wetting technique followed by drying and reduction at 130°C, Clarkson and Cirillo [16] report particle sizes in the range of 30 to 100 Å. Irrespective of the preparation method a minimum average size of about 60 Å for silver particles supported on SiO_2 therefore seems to be quite general. For silica-supported group VIII metals much smaller particle sizes have been reported, e.g. 12 to 15 Å for Pt [17-19], 14 Å for Ir [20] and 11 Å for Rh [21]. Boronin et al. [22] established that the ultimate dispersion of Pt/SiO_2 catalysts prepared by an ion-exchange method is a function of the initial distribution of the adsorbed material. We think, however, that the minimum average particle size which can be obtained for a given metal-support combination depends mostly on the chemical nature of both constituents. The consistent value of the particle size of Ag/SiO_2 samples differently prepared is an illustrative example of this principle.

From work with evaporated metal films it is concluded that a high mobility of metal atoms and metal clusters over a non-metallic substrate leads to a low saturation density of stable metal nuclei, which corresponds to a large particle size for a fixed amount of metal [23]. We think metal particle formation by vapour deposition on films to be comparable with formation by reduction of metal ions on a support. In both cases a high mobility, reflecting

a weak metal-support interaction, leads to large metal particles. The mobility of metal particles over an oxidic substrate is strongly impeded by the presence of metal ions at the metal-substrate interface [23-25]. The degree of reduction of supported metal particles therefore is an important factor governing their mobility. It is suggested that the reducibility of the metal-support interface strongly affects the mobility and thereby the particle size during particle genesis. Taking Pt particles as an instance, the presence of platinum ions has been established by ESR techniques even after the reduction in H_2 at 350°C [26]. the platinum ions interact strongly with the support and stabilize the very small metal particles. Studying the reduction behaviour of silver-Y zeolites Beyer et al. [27] report the formation of highly dispersed Ag clusters containing unreduced silver (Ag_3^+) after reduction at low temperatures. High-temperature reduction led to large silver particles (200 Å) formed outside the zeolite lattice. In accordance with the ideas discussed in this paper, the authors write that the positive charge of the small Ag clusters, stabilized by the affinity of the Ag^+ ions for special sites in the zeolite, could well be responsible for their high dispersion. The interaction of silver ions with silica being weak, however, silver clusters will be easily reduced completely which leads to a high mobility and a relatively large particle size of silver on silica.

Enhancement of the dispersion of silver in supported catalysts asks for a stronger silver (ion)-support interaction. An increased interaction can be achieved either by using another support or modifying the original support. Modification of SiO_2 to enhance the interaction with silver has been applied since long to produce silver-on-glass mirrors. In the construction of mirrors glass is treated with $SnCl_2$ solution prior to the deposition of silver metal by a reduction method as described in this paper [28]. It is believed that very small Sn nuclei catalyze the reduction of the silver ions. We think, moreover, that the silver-glass interaction increases due to the presence of metallic Sn on a layer of non-stoichiometric SnO. Analogous phenomena have been reported for the enhanced interaction of Au with glass by a layer of non-stoichiometric bismuth oxide [29]. The idea to introduce a second metal to improve the interaction between SiO_2 and a IB metal, will be applied in a next paper to produce excellent silver bimetallic catalysts [30].

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