XPS study of the size effect in ethene epoxidation on supported silver catalysts

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Supported silver catalysts $(Ag/\alpha - Al_2O_3)$ with different particle sizes (100-1000 Å) have been prepared and studied by XPS. It has been shown that the increase in the ethene epoxidation rate with silver particle size (size effect) is accompanied by a decrease in the Ag $3d_{5/2}$ binding energy value. The variation in $E_b(Ag \ 3d_{5/2})$ cannot be explained in terms of a change in the metallic character of the silver (initial state effect), but seems to be determined by the differential charging of the supported silver. The latter effect originates from the easier screening of surface charge induced by photoemission on the silver particles owing to their internal conductivity, rather than that on the dielectric support. The correlation between the internal conductivity of supported silver particles and their catalytic activity is discussed in the context of possible mechanisms for ethene epoxidation.

Introduction

Studying small silver particles supported on α -alumina is of great importance because of their uniqueness as catalysts for epoxidation of ethene. Decreasing the Ag particle size has an economic incentive, but one must take into account the existence of a size effect on the catalytic activity of the small supported particles.

The dependence of catalytic activity on the sizes of metal particles (size effect) is one of the main features of supported catalysts, and, therefore, there have been a large number of investigations devoted to the study of this problem.¹⁻¹⁰ It has been shown that the rates of a great number of catalytic reactions change at very small sizes of supported particles (<20-50 Å).¹⁻⁴ A number of authors have tried to explain such behaviour by the metal–non-metal transition in small metal clusters. Indeed, physical methods of analysis such as XPS, UPS, STM and EXAFS indicate that the deviation of different spectral characteristics from those of the bulk are observed for sizes of metal particles <50 Å.^{2.5-7} A few studies have revealed a correlation between the deviation of the electronic properties of the supported metals from bulk ones and their catalytic activity.^{2,8–10}

Amongst the metal supported catalysts, silver occupies a unique position. The change of its catalytic properties takes place at much larger sizes of the supported metal particles than is usually observed.^{11–13} Despite some discrepancies one can state that the sharp increase in the specific catalytic activity of the silver catalysts occurs at sizes above 100–500 Å. It seems that these changes in epoxidation rate can not be caused by a metal–non-metal transition. Indeed, this transition occurs for silver particles within a typical size range as for other metals.^{5–7} One must therefore suppose other reasons cause the observed variation in the catalytic properties of supported silver. To study this problem, we have used X-ray photoelectron spectroscopy (XPS) which has proven to be a very useful technique in the characterization of supported particles.

We report an XPS study of Ag/Al_2O_3 catalysts prepared with a narrow size distribution of the supported silver particles and both valence-band and core-level spectra are analysed. The variation of XP spectral characteristics with particle size is correlated with the specific catalytic activity of these catalysts. Furthermore, we will present data on the influence of caesium, which is the main promoter in commercial silver catalysts.

Experimental

A VG Escalab high-pressure electron spectrometer was used to carry out this investigation. Before beginning the experiments, the spectrometer was calibrated against $E_{\rm b}({\rm Au} \ 4f_{7/2}) = 84.0 \ {\rm eV}$ and $E_{\rm b}({\rm Cu} \ 2p_{3/2}) = 932.6 \ {\rm eV}$.

Ag/Al₂O₃ supported catalysts with various silver particle sizes and an Ag(111) single crystal were used as samples in this study. To prepare the Ag/Al₂O₃ model catalysts we used α alumina with a specific area of 7 $m^2 \ g^{-1}$ and a solution of a silver complex with ethanolamine having a molar ratio Ag: $NH_2C_2H_4OH = 1:4$ prepared by adding ethanolamine to an aqueous solution of silver nitrate.¹⁴ Impregnation of the α-alumina with silver amine complexes followed by drying, reduction of the silver particles at T = 360 K in vacuo and calcination at T = 510 K led to the formation of metallic silver particles. This conclusion is based on X-ray synchrotron diffraction radiation (XRSDR) and transmission electron microscopy (TEM) data taken for the same catalysts which indicate that the phase composition of all samples corresponds to a-alumina and metallic silver.¹⁵ Cs-promoted catalysts were prepared by impregnating the supported Ag samples with Cs solution followed by drying at 360 K in vacuo and calcination at 510 K. This catalyst preparation method has been described in more detail previously.14 It should be noted that to avoid undesired impurities, all initial reagents for the preparation of catalysts and supports were of special purity grade or synthesized under conditions to exclude sample contamination. In consequence, XPS survey spectra of our samples contained only lines characteristic of the support (aluminium and oxygen), silver and carbon. A typical survey spectrum of a supported catalyst is shown in Fig. 1 (curve 1).

Variation in the Ag particle size from *ca.* 100 to 1000 Å was achieved by increasing the amount of supported silver by repeating the impregnation procedure. The Ag content was determined by atomic absorption and was varied from 0.4 to 13.8 mass%. The size of silver crystallites was determined both by oxygen chemisorption and by transmission electron microscopy. The histograms of these catalysts had a variation

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Fig. 1 Survey spectra of Ag/Al₂O₃ supported catalyst (1) and Ag(111) single crystal (2)

in particle size of <40%, *i.e.* a reasonably uniform size distribution was observed.^{14,15}

The rate of ethylene oxide formation was measured by the flow-recirculation method at P = 1 atm and T = 500 K. The initial reaction mixture consisted of 2% ethene, 7% oxygen and nitrogen as the balance. Table 1 presents results on catalytic testing of Ag/Al₂O₃ catalysts taken from the ref. 14, where the procedure of the catalytic activity measurement and all characteristics for the synthesized catalysts were described thoroughly. Here, we use only those data which demonstrate the influence of the mean particle size on the rate of ethene epoxidation and selectivity towards the key product, ethylene oxide. It should be noted that both the activity and the selectivity change with time. Activation of the catalysts occurred within a few hours, and afterwards a steady state was attained. We have studied both the fresh (before testing their catalytic properties) and activated (after attainment of the steady state) catalysts.

All samples of the supported catalysts were ground and mounted on the standard holder by means of double-sided adhesive tape. Al-K α radiation (hv = 1486.6 eV) was used to record both valence-band and core-level spectra. To calculate the charging effect for non-conductive samples such as Ag/Al₂O₃ we used a method of internal standardization, the Al 2p line being taken as an internal reference with a binding energy of 74.5 eV.¹⁶

The Ag(111) single crystal (Monocrystal Co., USA) with a diameter of 12 mm and thickness of 2 mm was welded to two thin tungsten wires that allowed us to use a heating rate of 2 K s⁻¹. The temperature was measured with a Pt–Pt/Rh thermocouple welded to the edge of the crystal. The Ag(111) crystal was cleaned by a standard high-vacuum cycle: ionic etching followed by O₂ adsorption for 10 min at P = 10 Pa

Table 1 Variation of the rates of ethene epoxidation $[R(C_2H_4O)]$ and selectivity (S) towards ethylene oxide with mean silver particle size [d(Ag)] for unpromoted Ag/Al₂O₃ supported catalysts

d(Ag)/Å	$R(C_2H_4O)/10^{17}$ molecules m ⁻² s ⁻¹	S (%)
160	0.18	7
220	0.21	8
400	2.0	22
560	6.3	47
1000	4.8	41

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and T = 470 K and subsequent annealing *in vacuo* up to 970 K. After a few repetitions of this cycle, no contamination was registered in the survey XPS spectra (Fig. 1, curve 2) and the surface was characterized by a sharp (1×1) low-energy electron diffraction (LEED) pattern.

Results

Fresh unpromoted catalysts

Fig. 2 shows valence band spectra of silver and an Ag $3d_{5/2}$ core level spectra for three freshly prepared catalysts with mean sizes of supported Ag particles of 160, 560 and 1000 Å. These sizes have been chosen in accordance with the catalytic data presented in Table 1, which indicate that a sharp increase in specific catalytic activity by more than an order of magnitude occurs for these catalysts in the size range 300–500. Hereafter, we use the terms small, medium and large for Ag particles with sizes of 160, 560 and 1000 Å, respectively. The valence band of the pure support, shown for comparison, is superimposed on the silver signal, and therefore it has been subtracted from the catalyst spectra in order to obtain the valence band of the supported silver.

One can see that increasing the sizes of the Ag particles from 160 to 1000 Å causes changes in the silver valence-band spectra. These are determined by the variation in the silver concentration for the different samples: from 0.5 to 13.8 mass%, respectively. Unfortunately, the silver mass concentration can not be used to recalibrate the spectra, since most of silver atoms do not contribute to the XPS signal. This statement is based on the fact that the XPS analysis depth (20–30 Å) is much smaller than the particle sizes used in this study (>100 Å). To tackle this problem we have used the relative intensities of the core-level Ag $3d_{5/2}$ spectra presented in the same Figure. It is seen that the Ag $3d_{5/2}$ intensity for the sample with small Ag particles is six and twelve times less than that for the medium and large particles, respectively.

In Fig. 3 the valence-band and Ag $3d_{5/2}$ spectra of the supported silver with small and medium particles are compared (the spectra for the small particles being multiplied by a factor of six). The 560 Å silver particles are large enough to lead to an increase in the rate of ethene epoxidation (Table 1). One can see that both the shape and width of the silver valence bands for both samples are identical. The position and full width at half maximum (FWHM) of the Ag $3d_{5/2}$ spectra also



Fig. 2 Valence-band difference spectra (top) and Ag $3d_{5/2}$ core level spectra (bottom) of fresh supported Ag catalysts with different mean sizes of metal particles. (1) 160 Å, (2) 560 Å and (3) 1000 Å. Also shown as a dashed curve is the valance band spectrum from clean Al_2O_3 .

coincide for these fresh catalysts. It should be noted however that the value of the Ag $3d_{5/2}$ binding energy for the supported silver (367.9 eV) in the samples is less than the corresponding value for bulk silver (368.2 eV).^{16,17} The same value of 368.2 eV was measured by us for the Ag(111) single crystal. The coincidence of Ag $3d_{5/2}$ core-level binding energies for the fresh catalysts with various particle sizes seems to indicate that no correlation is observed between XPS data and catalytic properties of these catalysts in the ethene epoxidation reaction. It should, however, be recalled that the measurement of the reaction rate is carried out after reaching the steady state, *i.e.* after some activation of the fresh catalysts under reaction conditions.

Activated unpromoted catalysts

Ag $3d_{5/2}$ spectra for the activated samples with small and medium silver particles are shown in Fig. 4 (dashed curves), the corresponding spectra of the fresh samples are also shown for comparison (solid curves). After activation, a shift of the Ag $3d_{5/2}$ spectrum to higher E_b (up to 368.3 eV) is observed for catalysts with small particles. The FWHM of the spectra remain unchanged, consistent with a shift of the whole corelevel line. The increase in E_b for Ag $3d_{5/2}$ above the value characteristic for metallic silver (368.2 eV) confirms that the lower binding energies observed for the fresh catalysts are genuine, and are not caused by a mistake in the reference level value used $[E_b(Al \ 2p) = 74.5 \ eV]$. Distinctive behaviour is revealed for the catalyst with medium Ag particles: activation does not change the Ag $3d_{5/2}$ spectrum (Fig. 4). Similarly, no changes were observed in the spectral characteristics of the



Fig. 3 Valence-band difference spectra (top) and Ag $3d_{5/2}$ core-level spectra (bottom) of fresh supported Ag catalysts with mean sizes of metal particles of 160 Å (---) and 560 Å (---). The spectra of the former is multiplied by a factor of six.

sample with large particles and so its Ag $3d_{5/2}$ spectra are not discussed.

Thus, the data for the activated samples (Fig. 4) indicate that the activation changes the position of the Ag $3d_{5/2}$ spectra, the nature of these changes depends on the silver par-



Fig. 4 Ag $3d_{5/2}$ core-level spectra of supported Ag catalysts with different mean sizes of metal particles measured before (----) and after (----) activation. (1) 160 Å and (2) 560 Å.



Fig. 5 Variation of ethene epoxidation rate (∇) and $E_{b}(\text{Ag 3d}_{5/2})$ (\Box) with mean sizes of metal particles measured for unpromoted Ag catalysts

ticle size. This conclusion is confirmed by the data of Fig. 5 which shows the dependence of $E_b(\text{Ag } 3d_{5/2})$ on Ag particle size not only for the above samples, but also for other investigated catalysts. One can see that there is some threshold in the XPS characteristics of supported silver: small Ag particles in the activated samples have a much higher $E_b(\text{Ag } 3d_{5/2})$ values than the larger ones. We have juxtaposed the values of the ethene epoxidation reaction rate and $E_b(\text{Ag } 3d_{5/2})$ for several activated catalysts in Fig. 5. One can see a very good correlation between the catalytic activity and the XPS data: the lower the value of $E_b(\text{Ag } 3d_{5/2})$, the higher the rate of ethylene oxide formation.

Cs promoted catalysts

Analogous comparisons of the rate of ethene epoxidation and the binding energies of Ag $3d_{5/2}$ vs. caesium content for Cs promoted catalysts, as shown in Fig. 6, confirm this correlation. Indeed, when the caesium is doped in quantities larger than optimal a sharp decrease in the reaction rate is accompanied by an increase in $E_b(Ag 3d_{5/2})$ up to 368.3 eV. Thus, the correlation between the catalytic activity of the supported silver catalysts and the value of $E_b(Ag 3d_{5/2})$ seems to be general. However, before using this correlation it is necessary to understand what determines a decrease or an increase in the Ag $3d_{5/2}$ binding energies and, especially, their variation with Ag particle sizes (Fig. 5). The influence of caesium on the adsorptive and catalytic properties of silver will be discussed elsewhere.

Discussion

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The preparation of Ag/Al_2O_3 supported catalysts with a narrow particle size distribution has allowed us to measure a



Fig. 6 Variation of ethene epoxidation rate ($\mathbf{\nabla}$) and $E_{b}(Ag \ 3d_{5/2})$ (\Box) with Cs concentration measured for promoted Ag catalyst with 560 Å metal particles

more pronounced size effect in ethene epoxidation than previously reported in the literature.¹¹⁻¹³ It should be noted that the decrease in catalytic activity with decrease in particle size is accompanied by decrease in the selectivity towards ethylene oxide (Table 1). This phenomenon is explained by the fact that the rate of ethylene oxide formation on the catalysts with small silver particles becomes comparable with the rate of secondary oxidation of ethene on the support surface.¹⁸ The latter process together with direct total oxidation is responsible for the formation of CO₂, a byproduct of ethene oxidation. This suggestion is confirmed by an increase in the selectivity for the catalysts with small silver particles up to 25-30% when the alumina support is replaced by silica.14 These observations indicate that an analysis of the reasons causing the size effect is of great significance for silver catalysts.

The correlation between the rate of ethene epoxidation and the value of core-electron level binding energy seems to indicate the existence of a correlation between the catalytic and electronic properties of these catalysts and their variations with silver particle size. The particle size at which the electronic properties of small metal clusters become similar to those of the bulk metal has been discussed extensively, with silver having been the subject of a number of these reports. In particular, it has been shown that like other metals the bandwidth of the photoemission spectrum of the supported silver reaches its bulk value for Ag coverages of $\Theta = 2 \times 10^{19}$ atoms m^{-2} (*i.e.* particle size >20 Å).^{5,6} Similar conclusions about the critical size of Ag particles were made by Juska et al.¹⁹ who analysed changes in the modified Auger parameter upon high-vacuum Ag deposition on an alumina surface. Our data for fresh Ag supported catalysts are in agreement with this. Indeed, starting with Ag particles >100 Å in size, we have observed no variations either in the width of the Ag valence band or in the position or FWHM of the Ag $3d_{5/2}$ spectra (Fig. 3), i.e. all the fresh catalysts studied have identical electronic properties.

The lower value of the Ag $3d_{5/2}$ binding energy observed for the fresh samples (367.9 eV) compared with that for bulk silver (368.2 eV) can originate either from an initial state effect, when the chemical state of silver changes from metallic, or from a differential charging effect. Indeed, workers who have studied not only metallic silver, but also silver oxides by XPS,^{20,21} have demonstrated that, in contrast to many other metals, the oxidation of silver atoms decreases the Ag 3d_{5/2} binding energy value: the $E_b(Ag \ 3d_{5/2})$ values for Ag_2O and AgO are 367.7 and 367.4 eV, respectively. On the other hand, metal crystallites of between 50 and several hundred Å can exhibit the solid-state properties of a conductive metal that should provide easier compensation of the charge on their surface than that on the surface of a dielectric support. In consequence, the charging potential (ϕ) induced by photoemission will be less for the XPS lines of a metal compared with the charging potential on a dielectric support and so-called differential charging of a more conducting phase compared with a non-conducting one will appear; the XPS spectra of a metal will be negatively shifted by differential charging. The existence of differential charging for metal crystallites supported on a dielectric support has been revealed and thoroughly analysed by Barr^{22,23} who has shown that this shift can reach 1 eV. It is obvious that we have such a situation for our Ag/Al₂O₃ samples.

XPS parameters which do not depend on charging should be used to measure its contribution ($\Delta E_{\rm F}$) in the total variation of $E_{\rm b}$. One such methods is the application of a modified Auger parameter that represents the sum of a core-level binding energy and the kinetic energy of the corresponding Auger peak.^{23–26} Since the charging potential increases the core level binding energy and decreases the Auger kinetic energy by the same value, their sum is not changed with The corresponding Ag MNN Auger spectra of supported Ag for the fresh samples are centred at $E_{\rm k} = 358.4$ eV which gives a value of α of 726.3 eV. Comparison of this value with the known data for metallic Ag ($\alpha = 726.0-726.3$ eV) and for Ag oxides and other silver compounds ($\alpha = 724.0-724.5$ eV)^{16,24,25} indicates that the fresh samples contain metallic silver and, hence, the lower Ag $3d_{5/2}$ binding energies are most likely to originate from the differential charging effect.

Further confirmation of silver differential charging has been obtained by means of valence-band spectra which are sensitive both to the initial state and to relaxation effects.^{27,28} Fig. 7 compares the valence-band spectra of supported silver in a fresh sample and bulk Ag. For the bulk silver sample, we used an Ag(111) single crystal that had a good electrical contact, and, hence, electrochemical equilibrium with the spectrometer. One can see that the supported Ag has a valence band spectrum very similar to that of the single crystal, except for a shift of 0.8 eV to lower binding energies (Fig. 7). Indeed, a shift of the Ag(111) valence band spectrum by this value results in the coincidence of both shape and width of these spectra (Fig. 7) confirming our conclusion about the metallic state of Ag in the fresh catalysts.

The existence of differential charging in this system was also suggested by Juska *et al.*¹⁹ who studied Ag evaporation *in* vacuo onto a Al₂O₃ surface. They observed that E_b (Ag $3d_{5/2}$) which for small Ag coverages is higher than the bulk value, decreases to below the latter with increasing concentration of deposited silver and this difference is equal to 1.0 eV for Θ (Ag) > 10¹⁹ atoms m^{-2.19} Such behaviour contrasts with that of other metals (*e.g.* Pd and Cu) where the binding energy value of the metal core levels trends to the bulk value.^{27,29,30} Taking into also account the considerable variation of Ag $3d_{5/2}$ binding energies (up to 1 eV) observed for commercial catalysts³¹ one can state that differential charging is a general property of supported silver.

Then, it would be logical to suggest that the observed shift of the Ag $3d_{5/2}$ binding energy caused by the activation of the fresh sample with small silver particles (Fig. 4) originates also from the differential charging effect. The Ag MNN Auger spectra for fresh and the treated catalyst samples shown in Fig. 8 confirm this. Indeed, one can see that the shift of the XPS line (Fig. 8, top) is accompanied by the same shift of the

Fig. 7 Valence-band spectra of supported Ag catalyst with 560 Å metal particles (——) and an Ag(111) single crystal (–––)

binding energy/eV

4

6

8

10

0.8 eV

intensity (arb. units)



Fig. 8 Ag $3d_{5/2}$ (top) and Ag MNN (bottom) spectra of a supported silver catalyst with Ag particle size of 160 Å measured before (1) and after (2) activation

Auger line. In consequence, the Auger parameters coincide in both cases, and this shows the initial state of Ag in both samples is identical. The sensitivity of α to changes in the relaxation effect $(\Delta E_{\rm R} = \frac{1}{2}\Delta\alpha)^{23,24}$ allows us to conclude that relaxation shows essentially no contribution to the variation in the Ag $3d_{5/2}$ spectra. This is not surprising, since the relaxation shift is usually observed at much smaller sizes for supported metal particles (<20 Å)^{24,25} than the sizes used here (>100 Å). Thus, all presented data indicate that the studied samples contain metallic silver particles, and both lowering of $E_{\rm b}({\rm Ag \ 3d_{5/2}})$ values for the fresh samples and the shift of Ag $3d_{5/2}$ spectra for the treated samples with small Ag particles arise from the variation of the differential charging value of the supported silver. The variation of the differential charging value most likely originates from changes in the internal conductivity of the supported silver particles: the higher the internal conductivity of the Ag particle, the more effective is the compensation of its surface charge induced by photoemission, and the lower is the apparent binding energy value.

Comparison of the Ag $3d_{5/2}$ spectra for the fresh catalyst and Ag(111) single crystal made in Fig. 9 confirms the latter statement. Indeed, after artificial alignment of the Fermi levels of both the samples, the spectrum of the single crystal with high conductivity is centred at lower binding energy than that of the supported silver. Thus, the increase in $E_b(Ag \ 3d_{5/2})$ for Ag particles of size <400 Å (Fig. 5) indicates a lower internal conductivity compared to larger particles.

The existence of some transition in the conducting properties of supported Ag particles for sizes above 200–300 Å (Fig. 5) is also indicated from the NMR data: $^{32-34}$ the so-called



Fig. 9 Ag $3d_{5/2}$ spectra of a supported silver catalyst (2) and an Ag(111) single crystal (1). The spectrum of Ag(111) is shown after shifting by the differential charging value (0.8 eV) to lower $E_{\rm b}$.

Knight shift disappears upon decreasing the Ag particle size below 500 Å. The disappearance of the Knight shift which results from a hyperfine interaction of the Ag nuclei with conduction electrons is revealed by drastic broadening of ¹⁰⁹Ag NMR lines from Ag atoms located in the surface and subsurface layers of Ag particles.³²⁻³⁵ Theoretical calculation of the population of s-levels, their densities near the Fermi level and the Knight shifts for the surface and subsurface layers shows that for silver particles the influence of the surface propagates unexpectedly deeply into the inner layers of the Ag crystal (up to 200–250 Å, or 70–80 layers from the surface).³⁴ This behaviour is quite different from that for Pt particles, where the signal from the metal bulk was observed for considerably smaller mean particle sizes.³⁵ Therefore, both XPS and NMR data show that the conductive properties of Ag particles change significantly at a few 100 Å level.

There are two possible reasons for the variation of the conductivity of silver in an Ag(111) single crystal, catalysts with large Ag particles and catalysts with small particles. One possibility is changes of the inner silver morphology, the influence of which on the differential charging of metal crystallites has been shown by Barr.^{22,23} Alternatively, the presence of any contaminants in the supported Ag particles could also affect the conductivity of silver. In particular we should take into account oxygen because of the well known ability of silver to dissolve a large amount of oxygen into the bulk or subsurface layers.^{36,37} Furthermore, O₂ is one of the components of the reaction mixture.

Whichever of the factors, morphology or contamination, is the more significant, the revealed correlation between the ethene epoxidation rate and $E_{b}(Ag 3d_{5/2})$ means that samples of Ag with higher conductivity show higher activity in ethylene oxide formation. This conclusion is in accordance with the data of Campbell³⁸ who has shown that Ag single crystals have an activity greater by two orders of magnitude than supported silver. Obviously this is related to features of the mechanism of ethene epoxidation on silver. As shown in our previous studies, $^{39-41}$ to form ethylene oxide both 'ionic', and so-called 'covalent', oxygen should coexist at the silver surface. The 'covalent' oxygen is incorporated into ethene providing the formation of ethylene oxide, while the 'ionic' oxygen is necessary to create Ag⁺ ions (or surface silver oxide) as adsorption centres for ethene molecules.41 Formation of surface silver oxide requires the transfer of electron density from the silver to O atoms and higher conductivity of the Ag particles will facilitate this. More effective adsorption of ethene on these centres will in turn increase the total rate of ethene epoxidation. However, additional experiments are necessary to confirm this hypothesis.

Summary

We have revealed a correlation between the changes in the catalytic activity of supported silver catalysts and $E_{\rm b}({\rm Ag \ 3d_{5/2}})$ with Ag particle size. Relatively large Ag particles exhibit lower binding energies and a higher rate of ethene epoxidation than smaller (<500 Å) particles. These differences in E_b (Ag $3d_{5/2}$) values are most likely to result from the variations in differential charging of the supported silver which originate from the higher conductivity of Ag particles compared to the supporting surface. Measurements on an Ag(111) single crystal and comparison of its XPS spectra with those of the supported silver allowed us not only to prove the differential charging effect but also to determine its value. It is the differential charging that separates the silver particles with different surface potential and demonstrates the change in electronic properties of the silver with particle size. The revealed correlation between the internal conductivity of supported silver particles and their catalytic activity in ethene epoxidation is a general phenomonen, and can be used to characterize other silver catalysts.

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