Preparation of ZrO_2 on flat, conducting $SiO_2/Si(100)$ model supports by wet chemical techniques; X-ray photoelectron spectroscopy and Auger depth profiling

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Model supports consisting of a thin layer of SiO_2 on a silicon single crystal have been used to study $ZrO_2/SiO_2/Si$ model catalysts made by wet chemical preparation methods. Auger depth profiling and angle-dependent X-ray photoelectron spectroscopy show that catalysts prepared by a surface reaction between zirconium ethoxide and hydroxyl groups on the SiO_2 contain a highly dispersed zirconium phase that is converted to ZrO_2 upon calcination.

Keywords: ZrO_2/SiO_2; model catalysts; catalyst preparation; surface characterization; XPS; Auger depth profiling

1. Introduction

Zirconium oxide catalysts are of interest because of their catalytic activity for isosynthesis, methanol synthesis and catalytic cracking reactions. Zirconium oxide is also attractive as a support material because of its amphoteric character [1,2], but is impractical to use in unmodified form because of its low surface area. Stabilization of a highly dispersed zirconium oxide phase on a silica support is a possible route around this problem and is the subject of this work. We have recently reported on the preparation of such ZrO_2/SiO_2 systems by means of two methods: standard incipient wetness impregnation from an aqueous solution of zirconium nitrate, and a controlled surface reaction between zirconium ethoxide ligands and protons from hydroxyl groups on the SiO_2 support [3]. Heating in oxygen forms the desired zirconium oxide. The route via

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the ethoxide-hydroxyl reaction led to catalysts with a dispersion of around 75% and a favorable thermal stability.

Because of their surface sensitivity, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are particularly useful to look at differences in the dispersion and the chemical state of catalysts due to the preparation and pretreatment method. However, inhomogeneous sample charging is a severe problem with the ZrO_2/SiO_2 system because both materials are insulators. With a porous catalyst, charging shifts the position of the electron peaks by several electron volts with an accompanying distortion of peak shape. This complicates binding energy assignment and quantification.

Several authors [4–8] have found that detrimental charging can be avoided by using a model support consisting of a silicon or aluminum crystal with an oxidized layer of typically a few nanometers thickness on top. The active phase is usually deposited onto the support by evaporation [4–6] or by the decomposition of suitable metal carbonyls [7,8]. In this paper we use SiO_2/Si(100) model supports to study the formation of the active phase through wet chemical procedures which are standard in the preparation of porous catalysts. We use angle-resolved XPS as well as AES in combination with sputter depth profiling to study the effect of the preparation methods on the morphology of the eventual ZrO_2/SiO_2/Si(100) model catalyst. The results illustrate that with respect to surface analysis, flat, conducting model supports offer attractive advantages over porous supports. With the model supports one obtains spectra of much better resolution which, moreover, are easier to quantify owing to the flat geometry of the support. In particular, Auger depth profiling and take-off angle-dependent XPS become feasible because the direction perpendicular to the surface is defined.

2. Experimental

As a model support we used a silicon wafer (size approximately $5 \times 10 \times 0.1$ mm, surface orientation (100)), which has a 1.5 nm thick passivation layer of amorphous silicon oxide. The thickness of the oxide layer was determined with XPS using the relation:

$$\frac{I_{SiO_2}}{I_{Si}} = \frac{\sigma n_{SiO_2} \lambda_{SiO_2} (1 - e^{-d/\lambda_{SiO_2} \cos\theta})}{\sigma n_{Si} \lambda_{Si} e^{-d/\lambda_{SiO_2} \cos\theta}}$$

in which I_{Si} and I_{SiO_2} are the XPS intensities of the Si 2p peaks for the Si and the Si^{4+} components, n the atomic density, σ the cross section, λ_{Si} and λ_{SiO_2} the inelastic mean free paths of electrons at the prevalent kinetic energy through Si and SiO_2, respectively, θ the take-off angle with respect to the surface normal and d the thickness of the SiO_2 layer.

The impregnated model system was prepared by placing a drop of an aqueous solution of zirconium nitrate (BDH Chemicals Ltd) with a concentration of 0.045 g/l on the model support. This sample was allowed to dry in an evacuated dessicator. While the drop dried in such a manner that the edges were heavily loaded, the center of the sample was distributed more uniformly and this was the region chosen for study. The exchanged catalysts were prepared by soaking the silicon wafer in a solution of 2.4 g zirconium ethoxide (97%, Aldrich Chemicals), 20 ml ethanol and 1 ml acetic acid for 15 minutes at 340 K. This procedure allows the hydroxyl groups on the silicon wafer to react with the ethoxide ligands of zirconium. It is imperative to use water free ethanol in order to prevent precipitation of zirconium hydroxide. The samples were rinsed in ethanol at room temperature to remove unreacted ethoxide. Samples were oxidized in a tube furnace for 5 minutes at 775 K in a flow of 10% O_2 in N_2. A small chlorine contaminant corresponding to 0.1–0.3 of a monolayer, originating from the tube furnace, was detected with AES on a few of the samples after the oxidation treatment.

Auger spectra were measured in a Physical Electronics 550 spectrometer equipped with a double pass cylindrical mirror analyzer. Depth profiles were collected by bombarding the surface with 5 keV argon ions and simultaneously measuring the electron excited Auger spectra. The argon beam was rastered over an area of 6×6 mm around the point of impact of the electron beam (energy 3 keV, diameter approximately 1 mm). XPS spectra were obtained with a VG Escalab 200 spectrometer equipped with a monochromatized Al Kα source, a hemispherical analyzer connected to a five channel detector and a manipulator which enables one to vary the take-off angle between 0 and 90 degrees.

3. Results and discussion

Typical zirconium 3d doublet and silicon 2p and oxygen 2s single XPS peaks for the calcined powder and model catalysts, prepared via the zirconium ethoxide route, are shown in fig. 1. XPS parameters are given in table 1. The peaks in the spectra of the powder catalyst are broad and exhibit a charge shift of 7 eV. The spectra of fig. 1 have been corrected for this shift by using the Si 2p peak of SiO_2 at 103.4 eV as an internal reference for the binding energy [9]. The two components of the Zr 3d doublet are not resolved due to inhomogeneous charge broadening, which results in line widths on the order of 3.4 eV. If the Zr 3d signal is fitted with a doublet using a fixed $3d_{5/2}:3d_{3/2}$ intensity ratio of 60:40, a Zr $3d_{5/2}$ binding energy of 183.0 eV is obtained, which is in agreement with the presence of ZrO_2 [9].

The spectra of the model catalyst, obtained using the same instrument settings, show a much better resolution. The zirconium 3d doublet is resolved into its 5/2 and 3/2 components quite readily. The line width of the Zr $3d_{5/2}$

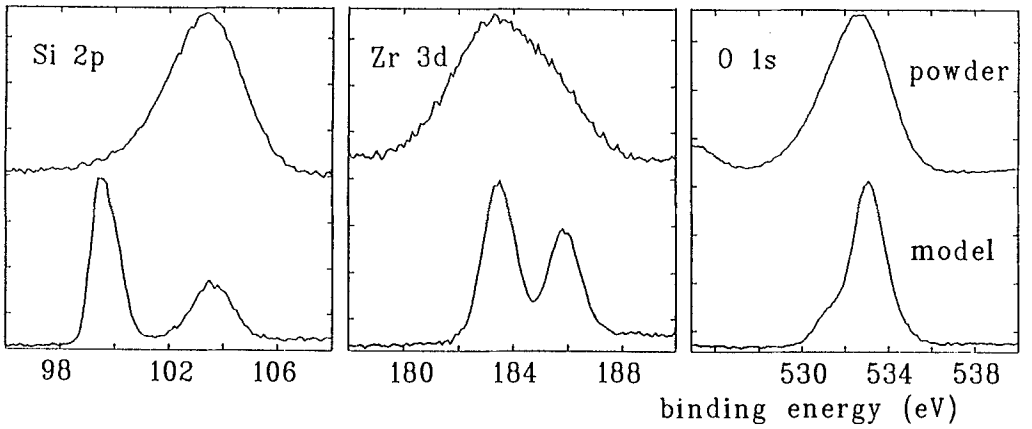

Fig. 1. XPS spectra of the Si 2p, Zr 3d and O 1s peaks of a calcined ZrO_2/SiO_2 powder catalyst (top) and a calcined ZrO_2/SiO_2/Si(100) model catalyst (bottom). The spectra of the powder catalyst have been corrected for charging.

peak is 1.4 eV, as compared to 3.3 eV in the spectrum of the powder catalyst. The Zr $3d_{5/2}$ binding energy in the spectrum of the model system of 183.3 eV is somewhat higher than the value found for the powder catalyst, but is characteristic of Zr^{4+}.

The O 1s spectrum contains two contributions. The dominant peak at a binding energy of 532.9 eV is characteristic of O^{2-} in SiO_2, the smaller peak at 531.0 eV is assigned to the ZrO_2. Note that the spectrum of the powder catalyst does not allow for a distinction between two types of oxide.

The Si 2p spectrum of the model catalyst consists of two peaks, one at 103.4 eV due to SiO_2 and the other at 99.5 eV due to the silicon substrate. The latter peak is actually an unresolved $2p_{3/2}$–$2p_{1/2}$ doublet, which is the reason that the Si 2p signal of the substrate is slightly asymmetric. The intensity ratio of the

Table 1
XPS parameters of the ZrO_2 catalysts

Peak	B.E. (eV)	FWHM (eV)	Assignment
powder catalyst			
Zr $3d_{5/2}$	183.0 [a]	3.3	Zr^{4+}
Si 2p	103.4 [a]	3.3	Si^{4+} of SiO_2
O 1s	532.6 [a]	3.4	O^{2-} of SiO_2
model catalyst			
Zr $3d_{5/2}$	183.3 [b]	1.4	Zr^{4+}
Si 2p	103.4 [b]	1.8	Si^{4+} of SiO_2
	99.5	1.1	Si° of Substrate
O 1s	532.9 [b]	1.8	O^{2-} of SiO_2
	531.0 [b]	1.8	O^{2-} of ZrO_2

[a] Corrected for a charge shift of 7 eV.
[b] Corrected for a charge shift of 0.2 eV.

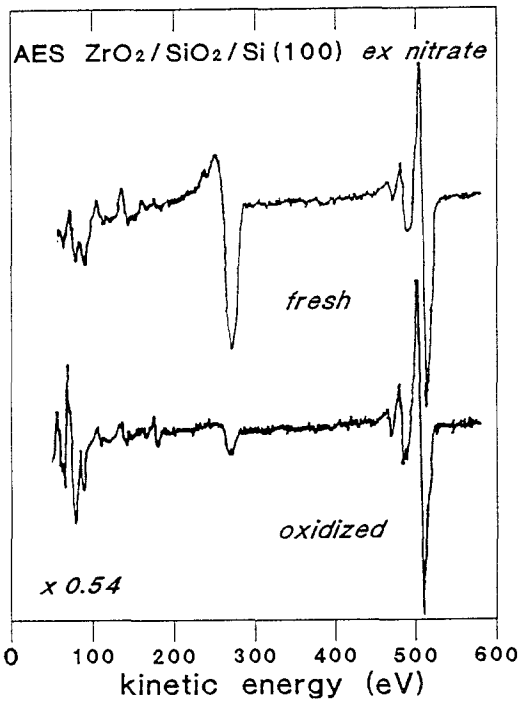

Fig. 2. Electron beam excited Auger spectra of the ZrO_2 model catalyst prepared by impregnation from a nitrate solution.

Si^{4+} and Si° peaks corresponds to an SiO_2 layer thickness of approximately 3 nm after calcination, as will be discussed in detail elsewhere [10].

The Zr $3d_{5/2}$ binding energy does not vary outside the limits of accuracy for the differently prepared model catalysts. Whether the model catalyst is prepared by exchange from zirconium ethoxide or by impregnation from zirconium nitrate, the binding energy is 183.3 ± 0.2 eV. The main difference between freshly prepared and calcined model catalysts is that the former contain a more intense C 1s signal (not shown), which disappears largely upon calcination.

Because the charging problem has been solved, Auger spectroscopy may be used to characterize the model catalysts. Fig. 2 shows Auger survey spectra of the fresh and the oxidized model catalysts prepared by impregnation from the zirconium nitrate solution. The spectra in fig. 2 show clearly the Si LMM Auger transitions at 76 and 92 eV of SiO_2 and Si, respectively, the Zr MNN transitions at about 115 and 145 eV, the C KVV transition at 272 eV and the O KVV transitions with the main peak at 503 eV.

The freshly impregnated catalyst is severely contaminated by carbon. Note that this carbon overlayer distorts the relative intensities of Si, Zr and O because of the energy dependence of the electron mean free path. Most of the carbon is removed upon oxidation. However, the Zr intensity decreases with respect to both Si and O in spite of the the removal of carbon. If we exclude

vaporization, this decrease in intensity indicates that a significant loss of dispersion occurs upon oxidation. Finally, the spectrum of the oxidized catalyst shows that the Si LMM peak at 76 eV has grown in comparison to that of the fresh catalyst, indicating that the SiO_2 layer has become thicker.

Auger spectra of similar quality were obtained from the model catalyst prepared from zirconium ethoxide. In this case, the relative Zr intensities before and after oxidation were about equal, indicating that the ethoxide-derived

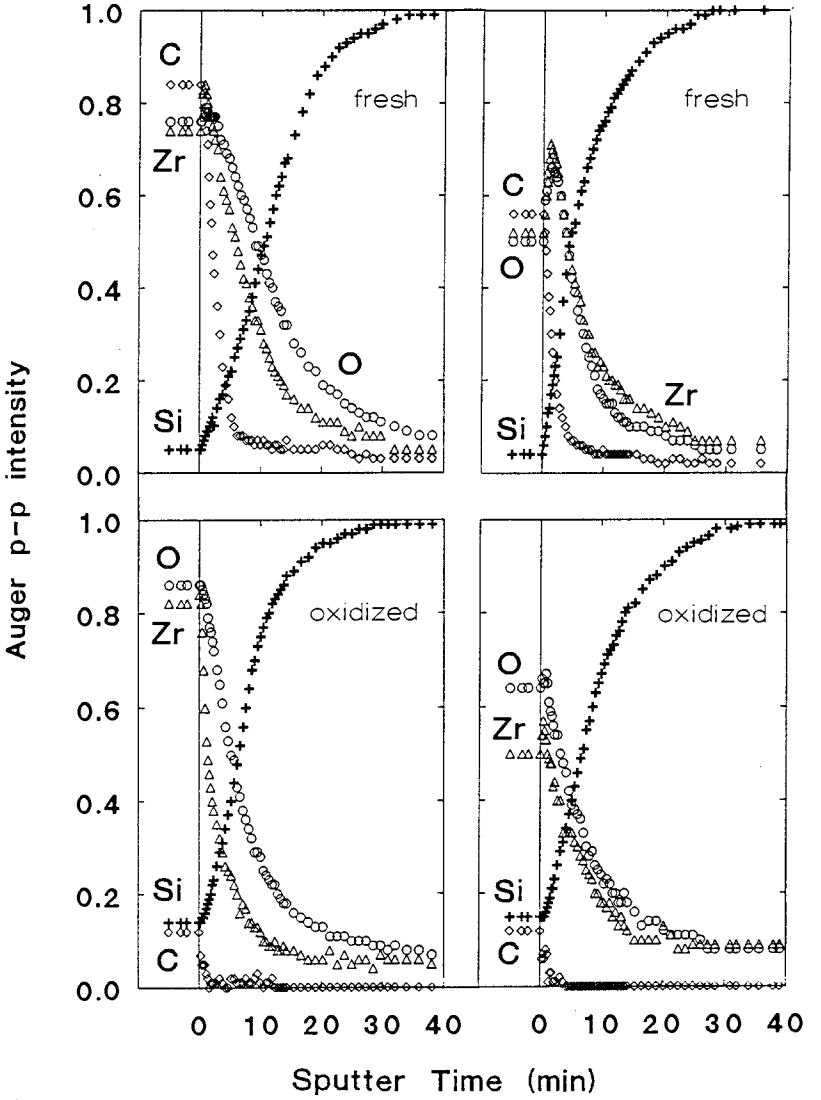

Fig. 3. Auger sputter depth profiles of freshly prepared (above) and oxidized (below) zirconium oxide model catalysts prepared from zirconium ethoxide (left) and zirconium nitrate (right). The following magnification factors were used: Si: 1x; O: 2x; C: 4x; Zr, above, left: 12x; below, left: 24x; right: 20x.

catalyst possesses a better thermal stability than the impregnated catalyst. This is in agreement with the results obtained with the porous silica-supported zirconia catalysts [3].

Since all elements of interest were readily detected by AES within a collection time of a few seconds, Auger depth profiling could be used to obtain concentrations as a function of depth. In fig. 3 the depth profiles are shown for the fresh and oxidized nitrate and ethoxide-derived model catalysts. Although all instrument settings were the same for each experiment, we can not guarantee that the sputter conditions were entirely identical, due to a small irreproducibility in the positioning of the sample. Hence, conclusions should not be based on absolute sputter times, but on changes in Auger intensities of the four elements with respect to each other. Since the intensities of each element are reported relative to the intensity of the clean silicon substrate (I^{∞}_{Si}), these intensities may be compared between the four experiments.

The relative time dependence of the zirconium and oxygen signals from the ethoxide-derived samples is markedly different from that of the nitrate-derived sample. The zirconium intensity has a much shorter half life than the oxygen intensity, for both the fresh and the oxidized ethoxide samples. This behavior is indicative of a layered structure in which the zirconium phase is on top of the silica layer. On the other hand, the normalized zirconium signal follows the oxygen signal almost identically for both of the nitrate-derived model catalysts. This and the steeper increase in the silicon intensity during sputtering indicate that the zirconium phase consists of relatively large particles which leave a large portion of the SiO_2 substrate uncovered.

As has already been discussed in connection with fig. 2, the freshly prepared catalysts are covered by a significant amount of carbon, which is removed by oxidation. However, the nature of the carbon layers on the two differently prepared fresh catalysts appears to be different. In the nitrate-derived zirconia catalyst the carbon is removed relatively fast by sputtering, and the Auger intensities of Zr and O go up significantly, and do not decrease until about 75% of the carbon is removed. This suggests that the carbon is present as a layer which covers the entire model catalyst. On the other hand, the carbonaceous layer on the fresh ethoxide-derived catalyst appears to be thicker, and mixed with zirconium and oxygen to a much higher extent, as suggested by the fact that the Zr and O signals increase only shortly initially and then decrease simultaneously with the C signal. Note, however, that the carbon is almost entirely removed when the Zr signal is still at 50% of its maximum intensity. This suggests that no ethoxide ligands are present at the level of the Zr-O-Si interface.

The carbon concentration of the oxidized catalysts is much smaller, and the carbon is removed rapidly upon sputtering. The sputtering profile of the oxidized catalyst prepared from zirconium ethoxide is characteristic of a layered system in which the thickness of the zirconia is probably smaller than that of the

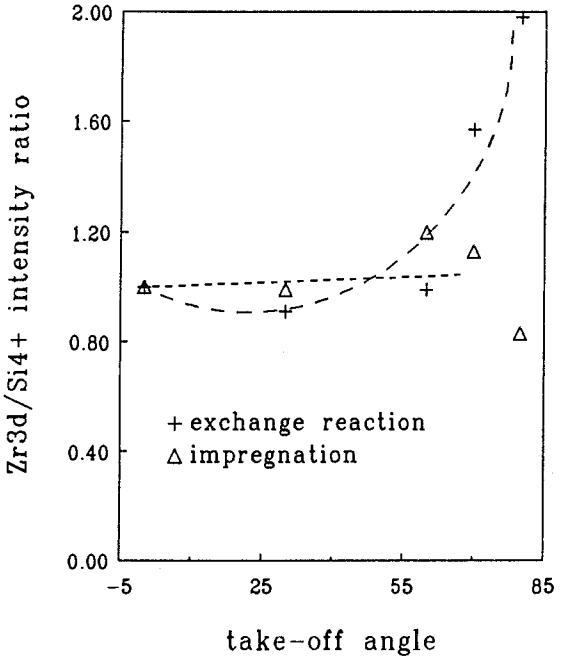

Fig. 4. Zr/Si XPS intensity ratios as a function of take-off angle for the ZrO_2 catalysts prepared by impregnation from nitrate solution and by the reaction between surface hydroxyl groups and zirconium ethoxide.

underlying silicon oxide layer. The depth profile of the oxidized zirconia catalyst prepared by impregnation, on the other hand, shows no features characteristic of layered structures. The simultaneous removal of Zr and O at a rate that compared to the increase in the Si signal is significantly slower than for the ethoxide derived catalyst, is consistent with the presence of poorly dispersed ZrO_2 particles which leave a considerable fraction of the support uncovered.

The conclusions from the Auger depth profiles can be verified qualitatively by take-off angle dependent XPS measurements. If a system forms a layer, its XPS intensity should increase with respect to that of the substrate when the spectrum is recorded at grazing angles. For a poorly dispersed phase the angle dependence should be less pronounced. Fig. 4 shows the Zr/Si XPS intensity ratio for the two differently prepared and subsequently oxidized zirconia model catalysts as a function of the take-off angle. Because the amount of Zr present on the two catalysts is not known and almost certainly not identical, we present both sets of Zr/Si ratios normalized to one at perpendicular collection angle. Fig. 4 clearly shows that the Zr/Si XPS intensity ratio for the catalyst prepared by impregnation hardly depends on the take-off angle, whereas the Zr/Si ratio for the exchanged catalyst increases significantly with increasing take-off angle. This again indicates that the exchanged catalyst has a high dispersion, whereas the

impregnated one has not. These conclusions are in good agreement with those obtained previously on silica-supported zirconia powder catalysts [3].

4. Conclusions

A flat, conducting model support consisting of a few nanometers of SiO_2 on a Si(100) substrate, offers attractive possibilities for the application of XPS, AES and other charge-sensitive surface spectroscopies, to study aspects of the surface chemistry involved in catalyst preparation. First, electrical charging is avoided, which means that not only the spectral resolution of XPS improves, but also that Auger spectroscopy becomes feasible. Second, the flat geometry of the support makes the application of sputter depth profiling and angle-dependent XPS and AES studies meaningful. These two techniques reveal that preparation of ZrO_2/SiO_2 catalysts by the reaction between the ligands of zirconium ethoxide and hydroxyl groups on the support leads to a well dispersed catalyst. Standard impregnation of SiO_2 with an aqueous solution of zirconium nitrate, however, leads to the formation of ZrO_2 particles which leave a considerable part of the SiO_2 surface uncovered.

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