# Structural Properties of Ag/TiO<sub>2</sub> Catalysts for Acrolein Hydrogenation

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We have successfully employed Ag/TiO<sub>2</sub> catalysts (metal loading, 7 wt %) in the gas-phase hydrogenation of acrolein, the  $\alpha,\beta$ -unsaturated aldehyde which is the most difficult to hydrogenate at the carbonyl group. The relations of the structural characteristics and surface state of these catalysts with respect to their activity and selectivity have been studied by surface analytical techniques (XPS, UPS, ISS) and magnetic resonance (ESR). The catalysts, consisting of titania-supported silver nanoparticles of less than 3 nm mean size, have been formed by various pretreatment procedures including low-temperature reduction at 473 K (LTR) and high-temperature reduction at 700 or 773 K (HTR). The unexpected finding of smaller silver nanoparticles of  $\approx 1.5$  nm mean diameter upon high-temperature reduction as compared to  $\approx 3$  nm mean diameter upon low-temperature reduction points to growth inhibition by Ti suboxide overlayers (several atomic layers thick) due to strong metal-support interaction, being the more pronounced the higher the reduction temperature applied. This interaction also leads to a truncated particle morphology deviating from spherical shape. The effect of both increasing particle coverage by TiO<sub>x</sub> and decreasing particle size, as obtained by high-temperature reduction, results in a decrease of the catalyst activity and selectivity to allyl alcohol. This behavior and the absence of  $Ti^{3+}$  at the very catalyst surface point to the fact that, different from the case of catalysts such as  $Pt/TiO_2$ ,  $TiO_3/Ti^{3+}$  species do not act as special sites for carbonyl group activation with our Ag/TiO<sub>2</sub> catalysts. With the LTR catalyst, the specific activity was 1 order of magnitude higher, compared to the HTR catalyst, and was accompanied by the formation of allyl alcohol with a much larger selectivity (LTR, 42%; HTR, 27%).

## 1. Introduction

Metal nanoparticles with their high dispersion, that is, the ratio of the number of surface atoms to the total number of atoms, may be employed in heterogeneous catalysts to facilitate thermodynamically feasible chemical reactions which are not known so far or proceed with poor selectivity. Over the past few years, we have found excellent properties of silver catalysts comprising silver nanoparticles on oxidic supports (SiO<sub>2</sub>, TiO<sub>2</sub>) applied to the hydrogenation of a C=O group in the presence of a C=C bond,  $^{1-4}$  in spite of their almost exclusive application in the chemical industry to catalyze oxidation reactions. Among the supports, TiO<sub>2</sub> is of special interest because the catalytic properties of dispersed metals can be modified by metal-support interactions. On the basis of the structural characterization by transmission electron microscopy (TEM) of Ag/TiO<sub>2</sub> catalysts employed in the hydrogenation of crotonaldehyde presented in a previous paper,<sup>4</sup> the same catalysts now have been applied for acrolein hydrogenation. Acrolein is considered to be the  $\alpha,\beta$ unsaturated aldehyde most difficult to hydrogenate to the allylic alcohol because of the lack of space-filling substituents at the C=C group.<sup>1,3,5,8-10</sup> By combination of surface structural characterization with chemical reaction investigation, a more

detailed understanding of the catalytic properties of these silver catalysts for hydrogenation reactions shall be achieved. With the  $\alpha$ , $\beta$ -unsaturated aldehyde crotonaldehyde (2-butenal) the selectivity to the desired allylic alcohol was entirely different from that of conventional hydrogenation catalysts comprising group 8–10 metals on nonreducible supports. The latter do not produce unsaturated alcohols as the main product in gas-phase hydrogenation.<sup>5–10</sup>

The ultimate size of the Ag particles depends on metal loading as well as the activation conditions. Interestingly, it was found that silver particles formed on titania by calcination and subsequent H<sub>2</sub> reduction at 473 K (low-temperature reduction, LTR) or at 773 K (high-temperature reduction, HTR) exhibit a rather narrow size distribution and very low mean particle sizes of  $d_{Ag} = 2.8 \pm 1.9$  nm for Ag/TiO<sub>2</sub>-LTR, and  $d_{Ag} = 1.4 \pm$ 0.5 nm for Ag/TiO2-HTR, that is, an exceedingly high dispersion ( $D_{Ag} = 0.46$  and 0.69, respectively).<sup>4</sup> The LTR catalyst produced a higher selectivity to crotyl alcohol (53%) than the ultradispersed HTR catalyst (28%). It was concluded that this pronounced change in selectivity qualifies the hydrogenation of crotonaldehyde over these Ag/TiO<sub>2</sub> catalysts as structure sensitive with the rate-determining step depending critically on the silver particle size and thus on the silver surface structure.

The crystalline nature of the oxide support enabled us to detect by high-resolution electron microscopy (HREM) thin amorphous layers covering the titania grains as well as part of the silver particles, being in close contact to the titania support,

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for both catalysts, Ag/TiO<sub>2</sub>-HTR and Ag/TiO<sub>2</sub>-LTR.<sup>4</sup> Although in the LTR catalyst the silver particles were only partly covered by these amorphous layers, in the HTR catalyst they were occasionally completely embedded. The amorphous layers, the nature of which remains unclear so far, were more closed and markedly thicker in the HTR catalyst. This makes the estimation of catalyst structure-reactivity relationships more complicated than it would be anyway because a distribution of particle sizes must be considered instead of mathematical models based on regular small crystallites.<sup>11</sup>

Therefore, the present work is aimed at a more thorough study of structural characteristics and surface properties of these catalysts with respect to their activity and selectivity by surface analytical techniques and electron spin resonance (ESR). X-ray photoemission spectroscopy (XPS) has been applied to obtain information on the chemical environment of surface atoms, in particular the oxidation state of silver loaded to the oxide support. Ultraviolet photoemission spectroscopy (UPS) has been used to study the valence band structure of surface species, and ion-scattering spectroscopy (ISS) has been employed to examine the chemical composition of the outermost surface layer. In addition to the previous TEM observations, ESR measurements have been performed to estimate the approximate size of particles from conduction electron spin resonance (CESR) signals because these particle sizes should be in a range where it should be possible to observe CESR. This phenomenon is based on the occurrence of quantum size effects  $(QSE)^{12}$  at extremely small particles and clusters, the magnetic and electronic properties of which differ markedly from those of the bulk material since their conduction electron band is split into discrete energy levels.13 Besides, ESR signals with hyperfine structure (hfs) may arise from other silver species such as Ag<sup>2+</sup> ions and/or charged clusters of only a very few silver atoms because of the coupling of the electron spin with the nuclear spin of silver, being 1/2. Furthermore, intrinsic paramagnetic centers of the  $TiO_2$  support such as  $Ti^{3+}$ , charged anion vacancies (F-centers), or impurities of other metal ions could give rise to additional ESR signals.

#### 2. Experimental Section

The Ag/TiO<sub>2</sub> catalysts (metal loading 7 wt % Ag) have been prepared by incipient wetness impregnation as described elsewhere<sup>4</sup> using AgNO<sub>3</sub> (Fluka) as the silver precursor and TiO<sub>2</sub> (P25 from Degussa, phase composition of 65 wt % anatase and 35 wt % rutile,  $S_{\text{BET}}$  of the catalyst: 36 m<sup>2</sup> g<sup>-1</sup>) as the support. After calcination in flowing air at 673 K (50 mL min<sup>-1</sup>) reduction in flowing hydrogen (3 h, 50 mL min<sup>-1</sup>) was applied either at 473 K (catalyst Ag/TiO<sub>2</sub>-LTR) or at 773 K (catalyst Ag/TiO<sub>2</sub>-HTR).

2.1. Surface Analysis. Surface analytical measurements were performed by means of a Leybold LHS 10 spectrometer, equipped with an EA 10/100 multichannel detector (Specs) on Ag/TiO<sub>2</sub> samples after 3 h reduction in flowing  $H_2/N_2$  gas mixture (20 vol % H<sub>2</sub>) either at 473 K or at 700 K with sample transfer into the spectrometer without exposure to the ambient atmosphere. The high-temperature reduction was limited for instrumental reasons to 700 K (designated as HTR'), somewhat lower than that applied for the HTR catalyst. Although usually calcined Ag/TiO<sub>2</sub> samples were employed in these experiments including the reduction treatment described above, in one case a catalyst sample that had been reduced previously in hydrogen at 773 K and stored in ambient atmosphere over several months (designated as "HTR-and-stored") was rereduced at 700 K prior to surface analysis. These activation conditions matched that employed prior to the catalytic reaction (see below).

For XPS measurements Mg K $\alpha$  radiation (1.2536 keV, 12 kV \* 20 mA) was utilized, and spectra were recorded at a pass energy (PE) of 35.5 eV. During XPS data accumulation for signal statistics improvement, a continuously changing surface charge was observed, in particular during the first hours, resulting in line broadening and erroneous binding energies without countermeasure. Therefore, these data were employed only if the shift of the binding energy scale was less than 0.2 eV within the data acquisition period. The data were usually measured with samples at room temperature, but in one case, a measurement was performed at a sample temperature of 823 K in order to decide about a suspected differential charging between the Ag metal particles and the TiO<sub>2</sub> support, because under these conditions, the surface charge is largely removed.

For UPS measurements HeII irradiation (40.82 eV) was utilized, and spectra were recorded at a PE of 23.7 eV with the samples held at elevated temperatures (at least 673 K, mostly 823 K) to remove the surface charge.<sup>14</sup> Thermal treatment for measuring purposes at 823 K in ultrahigh vacuum (UHV), also applied to one XPS measurement, may be considered as a kind of thermoevacuation pretreatment for some subsequently performed ISS measurements.

As final step of any measurement sequence, ISS sputter series were performed using 1 keV He<sup>+</sup> ions at 1 or 0.3 mA emission current (analyzer PE, 192 eV; scattering angle, 135°) where surface charges in general were neutralized by means of an electron flood gun. Spectra were recorded over an extended period of time to analyze the variation of the elemental peaks with sputtering time. Under these conditions the amount of sputtered material is estimated to about one monolayer on average.

Data reduction included satellite deconvolution (Mg K $\alpha$  satellites, HeII $\beta$  satellites) and integration of signal areas over a Shirley-type (XPS)<sup>15</sup> or a linear (ISS) background. Elemental ratios were calculated from XPS line intensity ratios using the Scofield ionization cross sections<sup>16</sup> together with an experimentally derived response function of the spectrometer to the variation of the photoelectron kinetic energy. The binding energies (BE) were first referenced to the line of adventitious carbon (C(1s) = 284.5 eV). Because this calibration did well reproduce the known Ti(2p<sub>3/2</sub>) BE of 458.7 eV for TiO<sub>2</sub>, except in one case where the whole BE scale appeared to be shifted, the Ti(2p<sub>3/2</sub>) line was employed as a secondary reference.

2.2. Electron Spin Resonance. ESR spectra were recorded by means of a ELEXSYS 500-10/12 CW spectrometer (Bruker) in X-band ( $\nu = 9.515$  GHz) at 77 and 293 K using a finger dewar as well as in Q-band ( $\nu = 34.033$  GHz) at 100 K using the Bruker variable temperature control unit. The magnetic field was measured with reference to a standard of 2,2-diphenyl-1picrylhydrazyl hydrate (DPPH). Reduction of as-calcined Ag/ TiO<sub>2</sub> samples was performed in flowing hydrogen (50 mL min<sup>-1</sup>) either at 473 K (Ag/TiO<sub>2</sub>-LTR) or at 773 K (Ag/TiO<sub>2</sub>-HTR) in an ESR flow cell consisting of two coaxial tubes similar to that described by Mesaros et al.<sup>17</sup> Subsequently, ESR spectra were recorded without exposure to ambient atmosphere. After recording the X-band spectra the samples were transferred into a side tube of 1.5 mm o.d. equipped to the flow cell and sealed off for recording the Q-band spectra. Simulation of ESR spectra was done by means of the program SIM14S of Lozos et al.<sup>18</sup>

**2.3. Catalytic Hydrogenation of Acrolein.** Gas-phase hydrogenation of acrolein (Aldrich) was carried out in a computercontrolled fixed-bed microreactor system which has been described in detail elsewhere.<sup>19</sup> This equipment allows the performance of high-pressure gas-phase hydrogenations of



Figure 1. X-band ESR spectra of (a)  $Ag/TiO_2-LTR$  calculated with parameters listed in Table 1, (b)  $Ag/TiO_2-LTR$  measured at 77 K, (c)  $Ag/TiO_2-LTR$  measured at 293 K, (d)  $TiO_2$  support without metal loading measured at 77 K, (e)  $Ag/TiO_2-HTR$  measured at 77 K, and (f)  $Ag/TiO_2-HTR$  measured at 293 K.

unsaturated organic compounds which are usually liquids with low vapor pressures at standard conditions (STP). The reactor effluents were analyzed on-line by an HP 5890 gas chromatograph, equipped with a flame ionization detector and a 30 m J&W DB-WAX capillary column. The respective silver catalysts were obtained by in situ reduction at the conditions described above. The reaction conditions for acrolein hydrogenation were as follows: temperature range 413 K < T < 553 K, total pressure p = 2 MPa, molar ratio H<sub>2</sub>/acrolein = 20, reciprocal space time  $W/F_{Ac,0} = 15.3 \text{ g}_{cat} \text{ h mol}^{-1}$  where W is the weight of catalyst and F is the molar feed flow of acrolein. These conditions and the catalyst particle size (0.2-0.4 mm) ensured that the catalyst was operated with negligible external or internal diffusion limitation of the reaction rate (effectiveness factor  $\eta$ > 0.95). In contrast to other supported catalysts (based, e.g., on Rh, Pt) for the hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes, there is only minor deactivation during the first 20 min in the case of silver catalysts. All given catalytic data (specific activities, selectivities) are based on steady-state behavior of the catalysts. The reproducibility of the catalytic measurements is  $\pm 2\%$  (with respect to the absolute value of conversion and selectivity). The selectivities of reaction products were calculated from moles of product formed per moles of acrolein converted. The catalyst activities were expressed as specific activities (on a gram of silver basis) and as turnover frequency (TOF) based on oxygen chemisorption and particle size measurements by TEM, respectively.

# 3. Results

**3.1. ESR.** At 77 K, both reduced samples, Ag/TiO<sub>2</sub>-LTR and Ag/TiO<sub>2</sub>-HTR, show anisotropic X-band ESR signals (see Figure 1 curves b and e). That of Ag/TiO<sub>2</sub>-HTR is mainly dominated by the Ti<sup>3+</sup> resonance.<sup>23</sup> The simulation (curve a in Figure 1) to fit the spectrum of sample Ag/TiO<sub>2</sub>-LTR considered contributions of various species as described by subspectra 1-4 in Table 1. Subspectrum 1 with axial g-tensor ( $g_{II} = 1.920$ ,  $g_{\perp} = 1.980$ ) assigned to Ti<sup>3+</sup>,<sup>23</sup> occurs also in the experimental spectrum of the unloaded support after hydrogen treatment at 773 K (curve d in Figure 1), although it is markedly weaker than in the silver-loaded catalyst (intensity ratio 0.03:1), but



**Figure 2.** Q-band ESR spectra of (a)  $Ag/TiO_2$ -LTR calculated with parameters listed in Table 1, (b)  $Ag/TiO_2$ -LTR measured at 100 K,

TABLE 1: Parameters Applied in Calculations of X- and Q-Band ESR Spectra of Ag/TiO<sub>2</sub>-LTR Shown in Figures 1a and 2a (See Text for Subspectra Details): Relative Intensity  $I_{\rm rel}$ , g-Tensor, Peak-to-Peak Line Width  $H_{\rm pp}$ , and Isotropic hfs Coupling Constant  $A_{\rm iso}$ 

and (c) unreduced Ag/TiO<sub>2</sub> measured at 100 K.

subspectrum										
no.	$I_{ m rel}$ /%	g-tensor	$\Delta H_{\rm pp}/{ m mT}$	$A_{\rm iso}/{ m mT}$	assignment					
X-Band										
1	7.4	1.974	1.2		Ti <sup>3+</sup>					
2	47.6	1.966	3.4		CESR					
3	44.6	1.935	8.0		CESR					
4	0.3	2.000	0.8	2.2	$Ag^{2+}$					
Q-Band										
1	1.6	2.007	5.5	9.4	$Mn^{2+}$					
2	0.1	2.010	0.5		<b>F-center</b>					
3	57.3	2.010	30.0		CESR					
4	41.0	1.930 (II)	12.0 (II)		Ti <sup>3+</sup>					
		1.980 (⊥)	9.0 (丄)							

not after reducing the unloaded support at 473 K. This suggests that the presence of silver favors the partial reduction of the TiO<sub>2</sub> support. The two superimposed isotropic singlets, subspectra 2 and 3, are assigned to CESR signals of silver nanoparticles reflecting the effect of a certain particle size distribution rather than that of two discrete particle size values. The origin of the doublet (subspectrum 4) on the low-field side could be due to the  $g_{\perp}$  part of isolated Ag<sup>2+</sup> cations ( $g_{\parallel} = 2.316$ ,  $g_{\perp} = 2.049$ ,  $A_{\parallel} = 3.66$  mT,  $A_{\perp} = 3.01$  mT<sup>24</sup>). However, the corresponding  $g_{\parallel}$  part is not detected, presumably due to low intensity and large line width.

At 293 K (see curves c and f in Figure 1) the Ti<sup>3+</sup> signal disappears in both samples because of short relaxation times. This behavior is well-known for Ti<sup>3+</sup> <sup>23</sup> and holds also for the CESR signals in sample Ag/TiO<sub>2</sub>-LTR. In contrast, a CESR line with  $\Delta H_{pp} = 2.7$  mT at g = 2.014 is still visible in the spectrum of sample Ag/TiO<sub>2</sub>-HTR, suggesting smaller silver nanoparticles in Ag/TiO<sub>2</sub>-HTR than in Ag/TiO<sub>2</sub>-LTR, since CESR signals of heavy metal particles are only visible at higher temperature if the particle size is small enough.<sup>20</sup> This result agrees properly with the findings by TEM (see Table 1).

The ESR spectrum of sample Ag/TiO<sub>2</sub>–LTR has also been recorded with better resolution in the Q-band at 100 K (see curve b in Figure 2). From the comparison of this spectrum with that of the unreduced sample (curve c in Figure 2) the formation of  $Ti^{3+}$  upon low-temperature reduction, in agreement with the

TABLE 2:	Results	of	Surface	Anal	lyses	Ex	periments
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		elemental ratio					
treatment	Ag(3d <sub>5/2</sub> )	Ag M <sub>5</sub> VV	$\alpha_{Ag}{}^a$	O(1s)	Ti(2p <sub>3/2</sub> )	Ag/Ti	Ti/O <sub>tot</sub> (Ti/O <sub>lat</sub> )
<b>HTR-and-stored</b> <sup>b</sup> (repetitive analysis)	367.8//1.80 367.8 <sub>5</sub> //1.77	357.7	725.4	530.0 <sup>e</sup> //1.88 529.8 <sup>e</sup> //1.73	458.7 <sup>g</sup> //1.82 458.7 <sup>g</sup> //1.62	0.17 0.17 <sub>5</sub>	$\begin{array}{c} 0.42 \ (0.48) \\ 0.39_5 \ (0.46_5) \end{array}$
<b>LTR</b> <sup><i>c</i></sup> (repetitive preparation) the same, measured at 823 K	367.6//2.10 367.5//1.03 367.7//1.07	358.45	725.85	530.0//2.10 529.9 <sub>5</sub> <sup>e</sup> //1.36 530.0//1.60	458.7 <sup>g</sup> //2.15 458.7 <sup>g</sup> //1.36 458.7 <sup>g</sup> //1.45	$\begin{array}{c} 0.068_5 \\ 0.048 \\ 0.043 \end{array}$	0.41 0.43 (0.50) 0.48
<b>HTR'</b> <sup><i>d</i></sup> (repetitive preparation)	367.5//2.25 367.5 <sub>5</sub> //1.90	358.35	725.9	530.0 <sup>f</sup> //2.44 529.8//2.10	458.7 <sup>g</sup> //2.51 458.7 <sup>g</sup> //1.95	0.038 0.054	0.44 (0.47) 0.41

 ${}^{a}\alpha_{Ag} = BE(Ag(3d_{5/2})) + KE(Ag M_5VV)$ .  ${}^{b}$  Reduction at 773 K (HTR) *plus* prolonged storage in ambient atmosphere.  ${}^{c}$  Unreduced sample followed by reduction at 473 K.  ${}^{d}$  HTR-and-stored *plus* reduction at 700 K.  ${}^{e}$  Minority signal at 531.5 eV (10–15% rel).  ${}^{f}$  Minority signal at 532.5 eV (7–10% rel).  ${}^{g}$  Reference energy.<sup>27</sup>



Figure 3. Ion-scattering spectra of sputter series from (a) Ag/TiO<sub>2</sub>-HTR-and-stored, (b) Ag/TiO<sub>2</sub>-LTR, and (c) Ag/TiO<sub>2</sub>-HTR'.

results of the X-band measurement (Figure 1), is properly evident. The hfs sextet is probably due to a  $Mn^{2+}$  impurity as suggested by the *g* value and the hfs constant.<sup>25</sup> Its low relative intensity and the superposition of other signals might be the reason it is not distinguished in the X-band measurements. The very narrow singlet at *g* = 2.010 could arise from F-centers as observed, too, in Au/TiO<sub>2</sub> catalysts.<sup>26</sup> Their concentration in sample Ag/TiO<sub>2</sub>-LTR is rather low as may be recognized from the small relative intensity value of the respective subsignal applied to the spectrum calculation (see Table 1).

**3.2. Surface Analysis.** The evaluation of XPS measurements yields binding energies, line widths (fwhm), and elemental ratios of the three types of Ag/TiO<sub>2</sub> catalysts as summarized in Table 2. The line widths are found to vary strongly, not only because of different reduction conditions, but also for repeated analysis or preparation of the same catalyst as well as measurement at 823 K. Scattering of spectral line widths has often been found with partially reduced TiO<sub>2</sub>-supported samples. Most likely, it is due to inhomogeneous defect distribution in the sample depending on the distance from the external surface which may lead to variations of conductivity and charging.

The O(1s) binding energy exhibits the value expected for TiO<sub>2</sub>. Some asymmetries could be accounted for by minor signals at 531.5 eV (OH groups) or  $\approx$ 532.5 eV (adsorbed water). The Ag(3d<sub>5/2</sub>) binding energies (367.5–367.8 eV) lay in all cases below those expected for metallic silver (368.3 eV) and even closer to the value known for Ag<sub>2</sub>O (367.8 eV).<sup>27</sup> To support the identification of the chemical state of silver species, the Ag M<sub>5</sub>VV Auger line was recorded as well. Besides differences in line widths, probably due to differential charging

effects resulting from inhomogeneous defect distribution in the support (see above), in addition a significant shift of the kinetic energies was observed indicating, via the silver Auger parameter, that in all cases the chemical state of the silver is close to metallic. Immediately upon reduction,  $\alpha_{Ag}$  almost coincides with the reference value (bulk silver  $\alpha_{Ag} = 726.1 \text{ eV}$ ),<sup>27</sup> whereas it is somewhat lower in the HTR-and-stored sample.

The Ti/O atomic ratios determined are very close to the expected ones provided the ratio is calculated using the signal for lattice oxygen (ca. 530 eV) only. Ag/Ti ratios of 0.17 were found with very good reproducibility in the HTR-and-stored sample. The measurements immediately upon reduction are less reproducible. They show a significant decrease of the Ag/Ti atomic ratio, which varies from an average of 0.046 for the HTR' sample to an average of 0.058 for the LTR sample, indicating a rather high sensitivity to the reduction conditions. Measurements at 823 K are not considered here for reasons discussed below.

Figure 3 shows ion-scattering spectra of the HTR-and-stored, LTR, and HTR' samples. In the HTR-and-stored sample (panel a), the silver peak is well developed already in scan 1 of the sputter series, although the Ti and O signals are very small. A small additional signal is visible slightly above 800 eV. This is an energy range where manganese, which has been traced by ESR, would be expected. After some scans, the overall intensity of the spectrum has increased and the ratio of the Ag and Ti signals has become smaller. This trend, continuing with prolonged data acquisition, is summarized in Figure 5, where the Ag/Ti area ratios of different runs are plotted versus the ion dose applied. In the LTR sample (panel b) the silver and



**Figure 4.** Ion-scattering spectra of sputter series, performed upon 823 K thermoevacuation, from (a)  $Ag/TiO_2$ -HTR-and-stored, and (b)  $Ag/TiO_2$ -LTR.



**Figure 5.** Intensity trends of Ag/Ti area ratios of ISS sputter series from  $Ag/TiO_2$  catalysts: (a) without thermoevacuation, and (b) upon 823 K thermoevacuation.

the titanium peaks are of comparable height from the very beginning, and the slight decrease of the Ag/Ti ratio with ongoing sputtering, which is found by peak integration (cf. Figure 5a), is not easily recognized from the spectra in view of the general intensity increase. In the HTR' sample (panel c) the silver peak is hardly visible at the beginning, but it increases with ongoing data acquisition and so does the Ag/Ti ratio.

Figure 4 shows ion-scattering spectra obtained with samples treated before at 823 K for UPS or XPS measurement. Remarkably, these spectra are very different from those of the other samples. Starting with the HTR-and-stored sample, the Ti signal, being much smaller than the Ag signal without thermoevacuation, is now comparable with the latter right from the first scan (compare panels a in Figures 3 and 4). Upon LTR (Figure 4b), the Ti signal is much higher after thermoevacuation and apparently now there is an increasing trend for the Ag/Ti ratio instead of a decreasing trend (compare Figures 3 and 4). In the spectra of Figure 4, the impurity peak at about 800 eV is well visible. The impurity obviously is only present in the outermost layer because it has practically disappeared at the end of the series.

Figure 5 summarizes the trends of the Ag/Ti ratio in the sputter series. The trends are plotted on a common ion dose scale in which one scan at 10 mA emission current was set equal to 3.3 scans at 3 mA emission current. It is quite clear that the Ag/Ti ratio is drastically reduced upon HTR' (Figure



**Figure 6.** Ultraviolet photoelectron spectra of  $Ag/TiO_2$  catalysts: (a) HTR', LTR, and HTR-and-stored samples together with bulk silver and (b) evolution of the spectrum at the beginning of data acquisition for a HTR-and-stored sample.

5a). Different from the decreasing trend of the Ag/Ti ratio in the HTR-and-stored sample, it is replaced by an increasing trend, which was well reproduced in two parallel experiments. Upon LTR, the Ag/Ti ratio is intermediate and there is still a slightly decreasing trend in the Ag/Ti ratio.

The ISS sputter series measured upon 823 K thermal treatment are summarized in Figure 5b. The Ag/Ti ratios are generally much smaller than for the other samples (note the different Ag/Ti scales in panels a and b). In the HTR-and-stored sample, the decreasing trend of the Ag/Ti ratio ends at half as large an ion dose and apparently turns to an increasing trend which, however, was not recorded long enough to prove its significance. On the other hand, it is quite obvious that upon LTR, an increasing trend is found nearly from the beginning.

Figure 6a shows UPS spectra measured with the samples discussed above and a spectrum of bulk silver for comparison.<sup>28</sup> They reflect the valence band of TiO<sub>2</sub> as a broad feature between 3.5 and 10 eV. A shoulder at about 11 eV occurs in the spectra of the HTR' and LTR samples. There are no well-defined signals that could be assigned to Ti<sup>3+</sup>, except in the HTR-and-stored sample where the valence band signal of TiO<sub>2</sub> seems to extend into a weak shoulder around 3 eV, which could, however, also arise from Ag<sup>+</sup> ions. No features to be assigned to silver metal are detected. In fact, the Fermi level intensity of silver is very low, and its d-band appears at the same binding energy as parts of the TiO<sub>2</sub> valence band. Figure 6b presents a series of spectra taken with a batch of the HTR-and-stored sample at 823 K, showing a broad signal between 15 and 11 eV, that can be assigned to adsorbed water.<sup>29</sup> It disappears gradually and leaves a weak shoulder at about 11 eV, which can be assigned to OH groups.

From the spectra displayed in Figure 6 it is clear that we cannot safely distinguish the signals of silver and of TiO<sub>2</sub> in UPS. Because of the weak silver Fermi level, the high intensity of the TiO<sub>2</sub> valence band strongly interferes with the attempt to single out the silver contribution. Changes in dispersion and/ or arrangement of silver aggregates could still cause modifications in the TiO<sub>2</sub> valence band shape, but only upon LTR is a slight difference observed. Most likely, the contribution of the Ag valence band intensity is low compared to that of the TiO<sub>2</sub> valence band earlier for Ag aggregates at the external surface of Na-Y zeolite.<sup>30</sup>

TABLE 3: Silver Particle Size, Dispersion, and Results of Acrolein Hydrogenation over Ag/TiO<sub>2</sub> Catalysts<sup>a</sup>

catalyst	$\bar{d}_{Ag} \pm \sigma$ , <sup>b</sup> [nm], TEM	D <sub>Ag</sub> , <sup>c</sup> TEM	$O/Ag^d$	activity [ $\mu$ mol g <sub>Ag</sub> <sup>-1</sup> s <sup>-1</sup> ]	$TOF/10^{-3}$ [s <sup>-1</sup> ] <sup>e</sup>	$TOF/10^{-3}$ [s <sup>-1</sup> ] <sup>f</sup>	S(C <sub>3</sub> H <sub>5</sub> OH) [%] <sup>g</sup>	$\begin{array}{c} {\rm S(PA)} \\ [\%]^h \end{array}$	$\begin{array}{c} {\rm S(PrOH)} \\ [\%]^i \end{array}$	S(HC) [%] <sup><i>j</i>,<i>k</i></sup>
Ag/TiO <sub>2</sub> -LTR	$\begin{array}{c} 2.8 \pm 1.9 \\ 1.4 \pm 0.5 \end{array}$	0.46	0.78	85.3	20.1	23.5	41.8	56.0	1.3	0.7
Ag/TiO <sub>2</sub> -HTR		0.69	0.56	9.8	1.5	3.7	27.2	68.3	1.3	0.6

<sup>*a*</sup> Reaction conditions: T = 473 K,  $p_{total} = 2$  MPa, molar ratio (H<sub>2</sub>/acrolein) = 20. <sup>*b*</sup> Mean value of silver particle diameter  $\pm$  standard deviation by TEM analysis.<sup>4</sup> <sup>*c*</sup> Silver dispersion by TEM analysis.<sup>4</sup> <sup>*d*</sup> Apparent silver dispersion by oxygen chemisorption.<sup>4</sup> <sup>*e*</sup> Turnover frequency based on  $D_{Ag}$  (TEM). <sup>*f*</sup> Turnover frequency based on O/Ag (chemisorption). <sup>*g*</sup> Selectivity to allyl alcohol. <sup>*h*</sup> Selectivity to propanal. <sup>*i*</sup> Selectivity to *n*-propanol. <sup>*j*</sup> Selectivity to C<sub>2</sub>-, C<sub>3</sub>-hydrocarbons. <sup>*k*</sup> Traces of acetone and *i*-PrOH account for the difference to 100%.





**3.3. Catalysis.** The hydrogenation of acrolein can proceed, in principle, via two parallel reaction pathways (see Scheme 1). Adsorption, activation, and subsequent hydrogenation of the C=O group results in production of allyl alcohol (propenol, reaction 1), which is the desired product from an industrial point of view. By hydrogenation of the C=C group in a parallel reaction, propionaldehyde (propanal, reaction 2) can also be formed. Furthermore, the formation of *n*-propanol as a result of the subsequent hydrogenation of allyl alcohol and/or propionaldehyde is also possible (reactions 3 and 4). Note that propionaldehyde can be produced principally by isomerization of allyl alcohol (reaction 5), too.

Table 3 summarizes the results of the hydrogenation of acrolein over both (LTR and HTR) titania-supported silver catalysts. The apparent activation energies estimated in the temperature range of 413 K < T < 553 K amount to  $32 \pm 1$  kJ mol<sup>-1</sup> and 59  $\pm$  3 kJ mol<sup>-1</sup> for the Ag/TiO<sub>2</sub>-LTR and Ag/ TiO<sub>2</sub>-HTR catalysts, respectively. With enhanced reduction temperature, that is, increased silver dispersion (from 0.46 to 0.69 as derived from earlier TEM results) and decreased silver particle size (from 2.8 to 1.4 nm as seen by TEM), the specific activities, on a gram of silver basis, and the turnover frequency (TOF), based on oxygen chemisorption and particle size measurements by TEM, are reduced by more than 1 order of magnitude. Simultaneously, a marked drop in selectivity to allyl alcohol was observed (from 41.8% to 27.2%), whereas the selectivity to propanal increased (from 56.0% to 68.3%). These results show that (i) the very demanding selective hydrogenation of acrolein to the desired unsaturated alcohol is not only possible with Ag/TiO<sub>2</sub> but proceeds with considerably high selectivity over the LTR catalyst and (ii) the reaction, as in the case of crotonaldehyde,<sup>4</sup> seems to be structure sensitive indicating that the rate-determining step depends critically on the silver particle size and, thus, on the silver surface structure. The selectivity to allyl alcohol (41.8%) is lower than the selectivity to the corresponding unsaturated alcohol in the hydrogenation of crotonaldehyde which gave a selectivity to crotyl alcohol of 53% over the LTR catalyst.

# 4. Discussion

**4.1. ESR.** As shown by Kawabata,<sup>13</sup> conduction electron spin resonance (CESR) can be observed in metal nanoparticles when

the spacing  $\delta$  of their energy levels is such large that  $\delta \gg h\nu$ and  $\delta \gg h/\tau$ , where *h* is the Planck constant,  $\nu$  is the microwave frequency, and  $\tau$  is the spin relaxation time. Then  $\delta$ , being inversely proportional to the particle volume, may be expressed by eq 1

$$\delta = (4E_{\rm F}/3N) \sim 1/d^3 \tag{1}$$

where  $E_{\rm F}$  is the Fermi energy of electrons, *N* is the number of conduction electrons, and d is the particle diameter.<sup>20</sup> From the peak-to-peak line width of the CESR signal,  $\Delta H_{\rm pp}$ , the diameter of the metal nanoparticle, may be derived according to (eq 2)<sup>21,22</sup>

$$\Delta H_{\rm pp} = v_{\rm F} (\Delta g_{\infty})^2 h \nu \gamma_{\rm e}^{-1} d^{-1} \delta^{-1}$$
(2)

where  $v_{\rm F}$  is the Fermi velocity of electrons,  $\Delta g_{\infty} = g$ (free electron) – g(silver) is the g-shift for the bulk metal, and  $\gamma_{\rm e}$  is the electron magnetogyric ratio. For silver the energy level spacing has been derived as  $\delta \ge 1.45 \times 10^{-18}$  K cm<sup>-3.20</sup> The g-shift for bulk silver was determined to  $\Delta g_{\infty} = -0.019.^{31}$  From these values together with  $v_{\rm F} = 10^6$  m s<sup>-1</sup>,  $\gamma_{\rm e} = 1.76 \times 10^{11}$  s<sup>-1</sup> T<sup>-1</sup>, and the microwave frequency of the X- and Q-band (9.515 and 34.033 GHz, respectively) the following expressions for the particle diameter are obtained:

$$d[m] = (\Delta H_{nn}[T] \ 1.546 \times 10^{-15})^{1/2}$$
 X-Band (3)

$$d[m] = (\Delta H_{\rm DD}[T] 4.32 \times 10^{-16})^{1/2}$$
 Q-Band (4)

From the peak-to-peak line width  $\Delta H_{pp} = 2.7$  mT of the Ag/ TiO<sub>2</sub>-HTR CESR signal measured at 293 K in the X-band (Figure 1f), a particle diameter of 2.0 nm results for this sample which reasonably agrees with the mean particle size of 1.4 nm found by TEM measurements.<sup>4</sup> For Ag/TiO<sub>2</sub>-LTR, CESR signals are found only in the spectrum measured at 77 K (Figure 1b), and the  $\Delta H_{\rm pp}$  are not as easily extracted because of a superposition of several signals. However, with the line widths of  $\Delta H_{pp} = 3.4$  mT and 8 mT taken from subsignals 2 and 3 of the calculated spectrum (Table 1, Figure 1a), eq 3 gives diameters of 2.3 and 3.5 nm agreeing well with the average size of silver catalyst particles obtained by TEM ( $d = (2.8 \pm$ 1.9) nm<sup>4</sup>), that is, with a broader particle size distribution than in the HTR sample. The values of the CESR g-tensor shift  $\Delta g$ =  $\Delta g_{\infty} - h/2\pi \delta \tau^{6}$  derived for samples Ag/TiO<sub>2</sub>-HTR ( $\Delta g$  = -0.012) and Ag/TiO<sub>2</sub>-LTR ( $\Delta g = 0.036$ ) from the experimental (Figure 1f) and the calculated spectrum (Table 1), respectively, differ from the value for bulk silver ( $\Delta g_{\infty}$  = -0.019) although  $h/2\pi\delta\tau$  tends to zero.<sup>31</sup> The reason may be a change of the spin-orbit coupling in Ag catalyst particles due to strong metal-support interaction.

Simulation of the Q-band spectrum at sample Ag/TiO<sub>2</sub>-LTR revealed that a rather broad isotropic singlet has to be superimposed over the remaining signals to achieve satisfactory agreement between the experimental and calculated spectrum

(Table 1, Figure 2a, subspectrum 3). This isotropic signal is assigned to the conduction electron spin resonance (CESR) of the Ag particles. From its line width of 30.0 mT (Table 1), a particle diameter of 3.6 nm results with eq 4, which agrees well with the larger diameter found from the X-band signals. It is also worth noting that neither a  $Ti^{3+}$  signal nor a silver CESR signal are observed in the as-calcined sample (Figure 2a) which confirms that both species are only formed upon reduction.

4.2. Surface Analysis. The intensity trends seen in the XPS, ISS, (and UPS) measurements give evidence of dynamic changes of the Ag/TiO<sub>2</sub> surface. In the HTR-and-stored sample very high Ag/Ti atomic and intensity ratios are found by XPS and ISS, respectively, (Table 2). In the course of the sputter series, the Ag/Ti ratio tends to decrease (Figure 5a), that is, the silver catalyst particles are predominantly exposed and situated on the very surface of the TiO<sub>2</sub> support. From the Kerkof-Moulijn intensity model for segregated particles on porous supports,<sup>32</sup> an average silver particle size of  $\approx 1.5$  nm can be estimated. For the Ag/TiO2-LTR sample a significantly lower Ag/Ti ratio was derived from both XPS and ISS, but in the ISS sputter series a decreasing trend still occurred (Figure 5a). Hence, the silver still is largely exposed, but less disperse: a mean particle size of 4.5 nm was estimated from the averaged XPS Ag/Ti intensity ratio. It should be noted, however, that these particle size estimates depend significantly on the choice of the photoelectron mean-free path,  $\lambda$ , that has been assumed to be 0.88 nm for Ag(3d) and 0.80 nm for Ti(2p).

In the Ag/TiO<sub>2</sub>-HTR' sample the situation is completely different. Although the Ag/Ti atomic ratio derived from XPS on average was only slightly below that of Ag/TiO<sub>2</sub>-LTR, the ISS-derived Ag/Ti intensity ratios are strongly diminished initially and, different from the other samples, they clearly increase during the sputter series (Figure 5a). This indicates that upon HTR' treatment the silver catalyst particles are largely covered by  $TiO_x$  species and that the  $TiO_x$  layer on silver particles is of considerable thickness. The increase of the Ag/ Ti ratio is very gradual and remains below 0.15, far from the values of  $\approx 0.8$  and 2 of the LTR and HTR-and-stored sample, respectively. Hence, on average the TiO<sub>x</sub> layer is assumed to be several atomic layers thick. Therefore, the slightly lower XPS-derived Ag/Ti atomic ratio points to silver particles buried under an oxide layer but not to increased particle size. On the contrary, because the  $TiO_x$  coverage is several atomic layers thick, a much larger attenuation of the Ag signal intensity should be expected if the Ag dispersion were the same as that upon LTR. Hence, the only marginal decrease of the Ag/Ti atomic ratio indicates significantly smaller silver particles upon HTR, in agreement with TEM<sup>4</sup> and ESR observations (see above). The nature of the amorphous layers, which remained unclear so far, is clarified now by means of the surface analysis experiments. The above findings also support the data of the oxygen chemisorption measurement (see Table 3), where an apparently lower dispersion was found for the HTR catalyst (O/Ag = 0.56), clearly resulting from the higher coverage of silver particles by amorphous  $TiO_x$ .

It can be assumed that because of reduction at 773 K the HTR-and-stored sample did initially show a TiO<sub>x</sub> coverage of silver catalyst particles quite similar to that of the HTR' sample. During storage in the ambient atmosphere the TiO<sub>x</sub> overlayer had obviously been removed leaving behind exposed silver particles of high dispersion (reversibility of the SMSI effect). The resulting mean particle size of about 1.5 nm does not necessarily correspond to that of the initial value upon HTR

since there are indications of partial reoxidation (see below). This might have been corrosively producing smaller particles. Nevertheless, taking into consideration a 1.5 nm initial mean particle size, an average thickness of about of 1.5 nm was estimated from the XPS Ag/Ti intensity ratio for the TiO<sub>x</sub> overlayer. Although this is only a rough estimate, being sensitive to the assumed Ag particle size as well as to the mean-free path data, it demonstrates that the XPS and ISS intensity trends observed upon HTR' can be rationalized best by a structure involving small Ag particles covered by several atomic layers of TiO<sub>x</sub>.

Upon thermal vacuum treatment at 823 K both the Ag/TiO<sub>2</sub>-HTR-and-stored and the Ag/TiO2-LTR sample exhibit a distinctly lower Ag/Ti ratio. This may result from a change in dispersion of the silver particles, for example, by growth and ripening and/or from a certain  $TiO_x$  coverage induced by strong metal support interaction. The latter is indicated by a slight increase of the Ag/Ti intensity ratio at the end of the HTRand-stored sputter series, more pronounced by the increasing trend of the Ag/Ti ratio of the LTR sputter series. This suggests that not only high-temperature treatment in hydrogen atmosphere, but also high-temperature treatment under UHV conditions (i.e., a much milder reduction than in hydrogen) can induce coverage of silver catalyst particles by  $TiO_x$ . It appears from this that the decoration of silver particles may occur under rather mild reduction conditions. The ease of  $TiO_x$  species movement onto the silver surface seems to be an effective means of growth inhibition in the process of particle formation.

Despite the clear proof by ESR of  $Ti^{3+}$  in LTR and even more in HTR silver catalyst samples as well as, but weaker, in the unloaded support upon high-temperature reduction, UPS did not give any evidence for the presence of  $Ti^{3+}$  at the very surface. The reduction of  $Ti^{4+}$  ions, favored by strong metal support interaction, obviously does not result in  $Ti^{3+}$  sites exposed to the vacuum. Although the detection of small amounts of  $Ti^{3+}$  among a majority of  $Ti^{4+}$  ions is difficult by XPS, it has been demonstrated<sup>48</sup> that they are easily proven by UPS in  $TiO_2$  single-crystal surfaces (produced, e.g., by ion bombardment). Therefore, the absence of any d<sup>1</sup> defect signal in the band gap after reduction at 700 K suggests that the majority of  $Ti^{3+}$  ions formed in the silver particle catalysts are concentrated near the interface between  $TiO_x$  coverage and particles where they are largely inaccessible for UPS measurements.

Although from XPS a significant Ag(3d<sub>5/2</sub>) binding energy shift was derived, the presence of metallic silver after reduction is clearly evidenced by the obtained Auger parameter  $\alpha_{Ag}$ , whereas the decreased Auger parameter in the HTR-and-stored sample may be due to partial oxidation of silver to Ag<sup>+</sup> ( $\alpha_{Ag}$  of Ag<sub>2</sub>O = 724.5 eV).<sup>27</sup> The latter might be also ascribed to a decreased core-hole screening in extremely small Ag particles which could have been formed by corrosive oxidation of larger ones, since upon HTR the Auger parameter is very close to that of bulk silver (cf. the HTR' value in Table 2). Hence, the presence of some Ag<sup>+</sup> in the HTR-and-stored sample can be quite safely concluded from the Auger parameter.

Deviations of the metal binding energy, as derived from XPS, of disperse, supported metal particles from the bulk value have been reported, for example, for Au/TiO<sub>2</sub> real catalysts,<sup>33–35</sup> but not for Ag/TiO<sub>2</sub>. On the other hand, deviations were not found for Au/TiO<sub>2</sub>(110) and Au/SiO<sub>2</sub> model catalysts.<sup>36</sup> Such differences have been ascribed to differential charging, initial-state and final-state effects due to the small number of atoms in the clusters (rehybridization, surface shifts, highly exposed atoms, reduced core-hole screening<sup>37–39</sup>), and specific support effects.

Differential charging, more likely with large particles than with small ones,<sup>30</sup> can be excluded considering the measurements at 823 K. At this temperature, the surface charge during data acquisition, which typically resulted in up to 5 eV binding energy shifts, was strongly reduced. In this regime,  $Ti(2p_{3/2})$ was found at 458.9 eV and Ag(3d<sub>3/2</sub>) at 367.9 eV. Specific effects due to particles containing only a small number of atoms should differ significantly between 1.5 and about 3 nm size, but we found no significant change of Ag binding energies with reduction temperature. Specific support effects leading to binding energy shifts for supported metal particles have often been demonstrated with zeolites.<sup>40,41</sup> They are thought to originate from different reasons,42,43 most recently to the electrostatic potential effects exerted by the support mainly via oxygen anions.<sup>44</sup> The extent of such effects should vary strongly between particles supported on the surface of and smaller ones largely embedded in TiO<sub>2</sub>. Hence, the binding energy shift observed can hardly be ascribed to these effects. We have also attempted to exclude possible influences of coadsorbates (H<sub>2</sub>O, OH groups), which can be detected by UPS and by XPS. However, the desorption of water as traced by UPS in Figure 6b had no influence on the Ag binding energy, and there was no difference between samples with or without OH signals detected by XPS (cf. Table 2). Thus, the reason for the binding energy shift of Ag/TiO<sub>2</sub> catalyst particles must remain unclear, as it is reported repeatedly, for example, for negative binding energy shifts of Cr(0) and W(0) on Al<sub>2</sub>O<sub>3</sub> by oxidic precursor reduction,<sup>45,46</sup> and Ag(0), Cu(0), Cr(0), and Rh(0) on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively, by vacuum deposition.<sup>47</sup>

4.3. Catalysis. The catalytic properties of the Ag/TiO<sub>2</sub> catalysts shall be discussed in terms of the results of the surface analyses described above and HRTEM,<sup>4</sup> in particular considering silver particles covered by  $TiO_x$  which may lead to new insights into the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes over silverbased catalysts. With high-temperature reduced titania-supported platinum catalysts an increase of both the activity per gram of Pt and the specific activity, expressed as TOF, was observed for the hydrogenation of acetone<sup>49</sup> and crotonaldehyde.<sup>50</sup> Moreover, also the selectivity to the allylic alcohol<sup>50,51</sup> was increased in the hydrogenation of the latter, and it was argued that high-temperature reduction of Pt/TiO<sub>2</sub> creates special active sites (Ti<sup>3+</sup>, oxygen vacancies) at the Pt metal/support interface which can activate the C=O group. This was supported by equal activation energies for LTR and HTR platinum catalysts, suggesting that the higher activity of the HTR catalysts is due to an increase in the number of active sites. However, this does not explain the catalytic behavior of the Ag/TiO<sub>2</sub> catalysts of the present study. Here, the activation energy of the HTR catalyst is distinctly higher than that of the LTR catalyst, and the lower catalyst activity at the higher reduction temperature results from several atomic layers of  $TiO_x$  covering the silver particles (see section 4.2.) which corresponds to the observed decrease of the apparent dispersion measured by oxygen chemisorption (O/Ag, Table 3). Remarkably, at the very surface of these overlayers predominantly Ti4+ ions are situated, whereas Ti3+ ions are concentrated near the interface between the overlayer and the Ag particles.

From the above physicochemical and kinetic findings it can be concluded that with our Ag/TiO<sub>2</sub> catalysts, different from catalysts such as Pt/TiO<sub>2</sub> and the suggested activation/ hydrogenation mechanism,<sup>50</sup> TiO<sub>x</sub>/Ti<sup>3+</sup> species do not act as special active sites for carbonyl group activation and enhanced hydrogenation according to the decreased selectivity to allyl alcohol as observed with the HTR catalyst. Thus, also the acrolein hydrogenation seems to be structure sensitive exhibiting an antipathetic behavior.<sup>52</sup> The larger fraction of Ag(111) faces of the LTR catalyst seems to lead to higher formation rates of allyl alcohol; thus it is supposed that the hydrogenation of the acrolein carbonyl group is favored by surface atoms on faces, as concluded for the hydrogenation of crotonaldehyde over these catalysts<sup>4</sup> and according to the hydrogenation of this  $\alpha$ , $\beta$ unsaturated aldehyde over silica-supported platinum particles.<sup>53</sup> Thereby, an ideal cuboctahedral particle shape is assumed to model the structure sensitivity.

In real catalysts, however, as we have recently shown for acrolein hydrogenation over supported gold catalysts, the occurrence of multiply twinned particles (MTPs) and the degree of particle rounding have a strong influence on the catalytic properties.<sup>54</sup> MTPs cause a lowering of both the selectivity to allyl alcohol and the turnover frequency. In our silver catalysts the particles do not exhibit a completely spherical shape, but are truncated, and to a certain extent multiply twinned particles occur even at very small size.<sup>4</sup> Thus, it cannot be ruled out that the decrease of the selectivity to allyl alcohol is due to multiple twinning and/or particle shape effects rather than to simple size effects. Therefore, the active site issue cannot be only treated by particle size variations, because the effects of faceting and multiple twinning may interfere. This opinion is supported by our recent findings about the surface modification of gold particles by a second metal (indium) that leads to a selective decoration of faces and leaves the edges free.<sup>55</sup> This approach was used to vary the active site characteristics of the gold catalysts. The active sites favoring the adsorption of the C=O group of acrolein and subsequent reaction to allyl alcohol have been identified as edges of gold nanoparticles. This concept cannot be straightforwardly transferred to the Ag/TiO<sub>2</sub> catalysts because with Au and the ZnO carrier, being not reducible by flowing hydrogen, no strong metal support interaction occurred.

# 5. Conclusions

The selective hydrogenation of acrolein on Ag/TiO2 catalysts has been proven as structure sensitive since TOF and allyl alcohol selectivity are distinctly lower for smaller Ag particles resulting from high-temperature reduction in comparison to the particles resulting from low-temperature reduction. The change in particle size is accompanied by a larger extent of particle coverage by  $TiO_x$  layers. This coverage, assumed to originate from strong metal-support interaction, is apparently formed already under relatively mild reduction conditions and therefore causes an effective inhibition of the growth of silver particles. Despite the clear proof by electron spin resonance of Ti<sup>3+</sup> ions present in the catalysts, in particular upon high-temperature reduction, no such species are found to be located at the very catalyst surface as revealed by ultraviolet photoelectron spectroscopy. Therefore, the active sites issue of these catalysts must be addressed by other structural features such as faceting, multiple twinning, or even selective coverage by TiO<sub>x</sub>.

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