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Key properties promoting high activity and stability of supported $PdSb/TiO_2$ catalysts in the acetoxylation of toluene to benzyl acetate

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ABSTRACT

The influence of thermal pretreatment in air, helium and $10\% H_2/He$ on the catalytic performance of a supported 9% Pd, 12% Sb/TiO₂ catalyst in the gas phase acetoxylation of toluene has been studied by integrated evaluation of catalytic tests and catalyst characterization using mainly XRD, TEM and XPS. A pretreatment temperature of 600 °C is beneficial for shortening the activation period, while the atmosphere during thermal pretreatment influences the long-term stability. Highest catalytic performance with a good long-term stability was reached with pretreatment in He, which creates Sb-containing Pd particles, on which a mixed Pd⁰/PdO surface is formed during time on stream. Sb stabilizes oxidized Pd species and leads to more stable catalysts in contrast to air-calcined samples. The catalyst pretreated in H₂/He was completely inactive, due to the formation of a stable Pd₈Sb₃ alloy.

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1. Introduction

Palladium particles supported on oxidic carriers are widely used as catalysts for a variety of heterogeneous catalytic processes, among them acetoxylation of hydrocarbons. Thus, acetoxylation of ethylene over supported Pd/SiO₂ is the most important technical process to produce vinyl acetate monomer [1]. In the case of toluene, acetoxylation with molecular oxygen [2–5] could be an attractive alternative for the production of benzyl acetate and its hydrolysis product benzyl alcohol, which is still based on the environmentally problematic chlorine chemistry [6] (Scheme 1).

So far, a catalyst with a nominal content of 10 wt.% Pd and 8 wt.% Sb supported on TiO₂ (anatase) has shown the best performance with 86% selectivity of benzyl acetate (BA) at 68.5% toluene conversion in the direct gas phase acetoxylation [2]. Remarkably, the activity of this catalyst increased dramatically within the initial 10–12 h on stream and this went along with a marked increase of the metal particle size. Unfortunately, this catalyst deactivated rather quickly after reaching the maximum toluene conversion at ca. 12 h. It has been shown that this deactivation can be effectively suppressed by doping with bismuth or copper. However, this led to a drop of the total activity and to a marked increase of the conditioning time [2,7]. For improving the industrial relevance of such catalysts, the conditioning time must be shortened and the catalyst stability must be increased while maintaining high activity and selectivity.

Inspired by these previous findings, we have recently performed a comprehensive study in which we explored the influence of different synthesis conditions and thermal pretreatment procedures on the nature of the Pd particles [8]. As a main result it was found that the conditioning time of a PdSb/TiO₂ catalyst can be markedly shortened, when the Pd particle size is purposefully increased prior to the catalytic test by a dedicated thermal pretreatment in He or 10% H₂/He atmosphere. Unfortunately, the catalytic activity of these catalysts was lower than that observed previously [2]. This may have been due to the formation of surface sulfides during thermal pretreatment in inert or reducing atmosphere, which was negligible in the earlier studies, in which the catalysts were calcined in air. These sulfides derived most probably from the reduction of ammonium sulfate which, according to the previous preparation procedure [2], was used as an additive to remove chloride (resulting from the SbCl₃ starting compound) during thermal treatment.

Therefore, we have developed a new synthesis procedure using Sb_2O_3 instead of $SbCl_3$ as starting material, which made the addition of ammonium sulfate dispensable. In this work, we show that thus prepared catalysts are much more active than those described in [8] and, moreover, show a remarkably high long-term stability, in contrast to previous catalysts [2] which deactivated rather quickly.

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2. Experimental

2.1. Catalyst preparation

Catalysts with a nominal content of 10 wt.% Pd and 16 wt.% Sb on TiO₂ (anatase, Kronos, containing about 2.3 wt.% S) were prepared in two steps with an intermediate calcination after the first step, in analogy to the procedure in Ref. [2]. While step 2 in both procedures is identical, Sb_2O_3 was used instead of $SbCl_3$ in the present procedure and no ammonium sulfate was added in step 1: (1) 1.9g of Sb₂O₃ powder (Sigma-Aldrich) was suspended in 20 ml distilled water and stirred for 20 min, thus, forming a homogeneous slurry. Then 8.2 g of TiO₂ were added to this suspension and stirred for 1 h at room temperature. Upon addition of TiO₂ the pH of the suspension dropped to 1. This is most probably due to the dissolution of traces of sulfate from the TiO₂ support as sulfuric acid. It should be mentioned that sulfur-free TiO₂ was also tested as support, however, led to inactive catalysts. Obviously, the surface acidity of sulfated TiO₂ is beneficial for the adsorption and conversion of toluene. Thus, 25% ammonia solution was added dropwisely to adjust pH = 7. The resulting suspension was heated at 70 °C for 1 h, followed by solvent removal in a rotary evaporator. The final solid was dried at 120 °C for 16 h and calcined in air at 400 °C for 3 h. (2) In the second step, 1.7 g PdCl₂ (>99.9%, Janapharm) was solved at 50 °C in 12.1 ml H₂O (acidified by HCl to pH = 1). Despite the fact that this introduces some chloride ions into the system, PdCl₂ was used as Pd source, since other Pd salts such as nitrate or acetate led to poorly active catalysts [8]. As was shown in our previous work, a small amount of chloride enables the intermediate formation of Pd chloro complexes which probably assist in the segregation of Pd metal particles [8]. After cooling to room temperature, pH = 4 was adjusted by dropwise addition of 1 N Na₂CO₃ (>99%, Alfa) solution, which results in the formation of $PdCl_4^{2-}$. Pd-Cl bond scission seems not to occur during this step, since no color change was observed and Pd remains coordinated by 4 Cl ligands in the PdCl₄^{2–} anions as it is the case, too, in solid PdCl₂. The calcined powder prepared in step 1 was added to the above solution and stirred for 1 h at room temperature, followed by solvent evaporation in a rotary evaporator. The resulting solid was dried at 120 °C for 16 h. For testing the influence of different thermal pretreatment procedures, one part of the sample was calcined in situ in the catalytic reactor prior to the catalytic test in a flow of 27.6 ml/min air at 300 °C for 2 h, according to the previously used pretreatment [2]. The remaining parts were pretreated for 4 h externally in an oven at 600 °C under (a) oxidizing (air, 50 ml/min), (b) inert (He, 50 ml/min) or (c) reducing (10%H₂/He, 50 ml/min) atmosphere. Highly purified (>99.99) gases were used for thermal treatment and for catalytic tests.

ICP-OES analysis of the final catalyst revealed a Pd and Sb content of 9.1% and 12.4% respectively, suggesting the loss of some volatile Sb during calcination in the first step.

2.2. Catalytic tests

Catalytic tests were performed in a fixed-bed Hastelloy C micro reactor at 210 °C and 2 bar total pressure with 0.8 g catalyst particles (0.425–0.6 mm). The catalyst particles were diluted with the fivefold amount of corundum particles to avoid hot spot formation during the reaction. The liquid reactants (toluene, >99.9%, Roth, Germany, and acetic acid, >99.9%, Walter CMP, Germany) in a molar ratio of 1:4) were dosed by a HPLC pump, while gases were dosed by mass flow controllers, resulting in a total feed mixture of toluene:acetic acid:oxygen:nitrogen = 1:4:3:16. Tests were performed with a gas hourly space velocity of GHSV = 2688 h⁻¹ and a residence time of τ = 1.34 s. The product stream was collected in a cold trap and analyzed off-line by gas chromatography (Shimadzu GC-2010) using an WCOT fused silica capillary column. The column outlet was connected to a methanizer (30% Ni/SiO₂ catalyst) for conversion of carbon containing products into methane, detected by a Flame Ionization Detector (FID).

2.3. Materials characterization

The elemental composition (Ti, Pd, Sb, Na, S) was determined by ICP-OES using a Varian 715-ES ICP-emission spectrometer. Prior to the analysis 10 mg of the sample was mixed with 5 ml of aqua regia and 3 ml hydrofluoric acid and treated in a microwave-assisted sample preparation system "MULTI WAVE" (Anton Paar/Perkin–Elmer) at \approx 200 °C and \approx 60 bar. The digested solution was filled up to 100 ml and measured. The data analysis was performed using the ICP Expert software. Carbon, hydrogen, nitrogen and sulfur analysis was done with the CHNS microanalysator TruSpec (Leco).

The surface area (S_{BET}) and pore size distribution of the catalysts were determined on an ASAP – 2010 (Micromeritics) by N₂ physisorption at –196 °C. Before the measurement, the catalyst was evacuated for 2 h at 150 °C to remove physisorbed water.

XRD powder patterns at ambient conditions were recorded in transmission geometry with Cu K α radiation (λ = 1.5406 Å) in the 2θ range of 10–55° (step width = 0.25°) on a Stoe STADI P diffractometer, equipped with a linear Position Sensitive Detector (PSD). Time per step was 25 s for the samples without Si as standard and 160 s with Si as standard). Processing and assignment of the powder patterns was done using the software WinXpow (Stoe) and the Powder Diffraction File (PDF) database of the International Centre of Diffraction Data (ICDD).

Transmission Electron Microscopy (TEM) investigations were carried out at 200 kV using a CM-20 microscope (Philips) equipped with an EDXS Noran Six (Thermo Scientific). Samples were prepared by depositing the catalysts on a nickel grid (300 mesh) coated with carbon film.

X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB 220iXL instrument with Al K α radiation (E = 1486.6 eV). The samples were fixed with a double adhesive carbon tape on a stainless steel sample holder. The peaks were fitted by Gaussian–Lorentzian curves after Shirley background subtraction. The electron binding energy was referenced to the Ti 2p_{3/2} peak of TiO₂ at 458.8 eV. For quantitative analysis of the near-surface region the peak areas were determined and divided by the element-specific Scofield factor and the analysator-depending transmission function.

3. Results

3.1. Catalytic tests

In Fig. 1 the catalytic performance of the 9Pd12Sb/TiO₂ catalyst obtained after the three different thermal pretreatment procedures (see Section 2.1) is compared. The catalytic performance after thermal pretreatment at 300 °C in air is similar to that of the conventionally prepared PdSb/TiO₂ catalyst from Ref. [2], which was



Fig. 1. Toluene conversion (X-Tol), selectivity (S-BA) and yield (Y-BA) of benzyl acetate during time on stream over the $9Pd12Sb/TiO_2$ catalyst pretreated (a) at 300 °C in air for 2 h, (b) at 600 °C in air for 4 h and (c) at 600 °C in helium for 4 h.

pretreated after the same procedure but prepared using SbCl₃ and $(NH_4)_2SO_4$. The maximum BA yields are continuously increasing and reach a maximum after about 10–12 h, followed by rapid deactivation. This confirms clearly that the new preparation method used in this work leads to equally effective catalysts as the conventional procedure used in Ref. [2].

A significant difference can be seen when precalcination in air is done at 600 °C. In this case, the conditioning period shortens to about 5–6 h during which the BA yield steeply increases and then reaches a plateau. The maximum BA selectivity is higher than after calcination at 300 °C (Fig. 1b). The main reason for the higher selectivity is most probably the less pronounced carbonization of toluene over the catalysts pretreated at 600 °C leading to a significantly lower amount of carbon deposits in the used samples (Table 1). Other byproducts are CO_2 and small traces of benzylaldehyde, benzylidene acetates and benzyl alcohol (selectivities between 0 and 2%). Equilibration time and maximum catalytic performance do not change when the atmosphere of the thermal pretreatment at 600 °C changes from air to He (Fig. 1c). However, a significant improvement of the catalyst stability is observed in the latter case, reflected by only a 10% drop of the BA yield within 24 h on stream. The most surprising effect was seen with a catalyst after thermal pretreatment in 10% H₂/He at 600 °C. This sample revealed to be totally inactive with a toluene conversion less than 1%. Therefore, these results are not plotted in Fig. 1.

From these results it is clearly evident that the thermal pretreatment has a significant impact on the catalytic performance. While the pretreatment temperature is crucial for the duration of catalyst equilibration, the surrounding atmosphere is more important for the BA selectivity as long as it has no reducing properties which lead to complete activity loss. To get deeper insights into this unexpected behavior, detailed characterization of catalysts was performed after thermal pretreatment, after reaching maximum catalytic performance at 9 h and 6 h on stream for samples calcined in air and He, respectively, and after 30 h on stream. For this purpose, the reaction feed was stopped and the system was cooled slowly to room temperature in inert atmosphere.

3.2. Catalyst characterization

3.2.1. Elemental analysis and surface area

Inspection of Table 1 shows that the Pd content of calcined and used catalysts is almost equal to the nominal value. In contrast, the corresponding Sb value after calcination is slightly lower, pointing to some loss of Sb as volatile species during thermal treatment, especially for the He treated samples. No further change in the Pd and Sb contents is observed during use in the reaction. A minimum percentage of 1.5% sulfur is still detected, which is however much smaller than the 6–7% detected in the catalysts of Ref. [8], in which $(NH_4)_2SO_4$ was used as additive. This small amount of residual sulfur is part of the TiO₂ support, yet it might not have a detrimental impact on the catalytic performance, since sulfur-free anatase, which has also been tested as support, does not lead to improved catalysts.

An interesting trend is observed for the BET surface areas (Table 1). A marked decrease of the surface area and pore volume of the pure support is evident upon loading with the metal components. This may be partly due to pore blocking of the support with the metal components. In addition, the intermediate calcination between step 1 and 2 in the preparation may also have affected the BET surface area. The decrease of the surface area and pore volume is partly reversible after calcination in air but not in helium at 600 °C. On the other hand, these values decrease again when the air-calcined sample is used in the acetoxylation reaction while only a slight effect is observed for the helium-pretreated catalyst. This suggests that high-temperature treatment in oxidizing atmosphere may have an impact on the support structure, most probably on the TiO₂ crystallite size which is smaller for the samples after air pretreatment (see supplementary data, Fig. S1 and XRD results below). This may be the main reason for the difference in the BET surface areas.

In former studies, coke deposition was found as main reason for the deactivation of the PdSb/TiO₂ catalysts [2]. Therefore, the amount of C was also analyzed in differently pretreated catalysts after different time on stream (Table 1). As expected, coke deposition increases with time on stream for all samples. The highest amount of carbon is found on the sample calcined at 300 °C, whereas for both samples treated at 600 °C nearly identical C contents were found, independent on the pretreatment atmosphere (Table 1). Nevertheless, the catalyst calcined in He at 600 °C is more stable than the one calcined in air at the same temperature (Fig. 1).

Table 1

Elemental composition, BET surface area and pore volume of 9Pd12Sb/TiO₂ catalysts after different thermal pretreatments given in brackets and corresponding spent samples after different time on stream. Sulfur content and surface area of pure TiO₂ is also shown.

Sample-time on stream	Pd	Sb	S	Na	С	BET-surface area (m ² /g)	Pore volume (cm ³ /g)
Pure TiO ₂	-	-	2.3	-	-	315	0.27
Fresh	9.1	12.4	1.5	5.3	-	56.6	0.12
(300°C-air)	7.7	10.5	1.3	4.6	-	81.5	0.14
(300 °C-air) – 32 h	8.1	9.7	1.6	5.3	4.25	64.6	0.10
(600°C-air)	8.5	12.2	1.4	5.1	-	115.3	0.38
(600 ° C-air) – 9 h	8.6	12.2	1.3	5.0	0.5	71.6	0.15
(600 ° C-air) -s 30 h	8.8	12.5	1.4	5.2	2.2	52.8	0.12
(600°C-He)	9.3	9.3	1.5	5.7	-	28.6	0.10
(600 ° C-He) – 6 h	8.2	10.2	1.6	5.9	0.65	40.6	0.13
(600°C-He) – 32 h	9.1	8.8	1.6	5.35	2.4	35.5	0.11

This suggests that coke formation is not the only reason for deactivation.

3.2.2. X-ray diffraction

The XRD patterns of all samples show of course the reflections of the anatase support [PDF No. 21-1272] besides those of Si which was used as an internal standard (Fig. 2a) for the exact determination of peak positions and intensity. Besides, some small traces of NaCl [PDF No. 5-628] and Na₂SO₄ [PDF No 75-914] are seen in certain samples, which might have formed from Na₂CO₃ and PdCl₂ or sulfate contained in the TiO₂ support, respectively. All XRD patterns of the spent samples and also of the fresh catalysts pretreated in He at 600 °C show clearly the presence of a metallic Pd phase [PDF No. 88-2335], while Pd in the fresh catalyst calcined in air at 600 °C is present as PdO [PDF No. 41-1107]. In contrast, when thermal pretreatment is performed in 10% H₂/He at 600 °C, no Pd but a Pd₈Sb₃ alloy phase [PDF No. 89-2059] is formed. The Full Width at Half Maximum (FWHM) of the anatase peaks is broader for the samples calcined in air, suggesting lower crystallites size. This is evident from Fig. S1 (supplementary data) in which the TiO₂ crystallite size, calculated by the Scherrer equation, for samples after thermal pretreatment in air and He is compared. This could be one reason for the higher BET surface area observed in the air-calcined sample (Table 1). In addition to TiO₂ crystallites, the changes of the BET surface described above can be explained also by the different Pd crystallite size. Very sharp Pd reflections indicating large crystallites were found for the sample after He pretreament with the lowest BET surface. The half widths of the Pd reflections after the different stages of use show no significant differences. This could explain why the BET surface areas of the samples pretreated in air and helium at 600 °C do not differ much after 30 h and 32 h on stream respectively (Table 1).

Significant differences are evident in the shape of the Pd (111) reflections, which have been deconvoluted into several subsignals (Fig. 2b). The position, intensity and FWHM of these signals are listed in Table 2. A single symmetric peak appears in the fresh sample after thermal pretreatment in He at 40.01°, which is consistent with the presence of a crystalline metallic Pd phase with cubic structure and a Fm-3m (225) space group [9]. After use in the catalytic reaction, this peak splits into three subsignals, which are all shifted to lower values of 2θ in comparison to the peak of pure metallic Pd. This behavior points to a change of the Pd lattice during time on stream, which is most probably caused by the incorporation of other components such as Sb, C and/or H. Thus, the dissolution of C [10,11] and H [12] into the Pd lattice led to slight downshifts of the 2θ values, as likewise observed in Fig. 2b, while this was not observed for oxygen. In the latter case, only surface or bulk Pd oxides were formed, the XRD reflections of which do not appear in the metallic Pd region [13-16]. TEM measurements shown below confirm the incorporation of Sb into the Pd lattice of the He-calcined sample. According to the phase diagram, incorporation of Sb into the Pd lattice is possible for Pd/Sb ratios higher than 5, while for Pd/Sb ratios between 3 and 0.5 stable alloy phases such as Pd₁Sb₂, Pd₁Sb₁, Pd₈Sb₃ and Pd₂₀Sb₇ are formed [17]. In our case, this happened when the sample was pretreated in reducing atmosphere, namely 10% H₂/He. In Fig. 2a the reflections of a Pd₈Sb₃ alloy phase are clearly seen after this treatment.

Inspection of the intensity of the Pd reflections of the Hepretreated catalyst after 6 h and 32 h on stream (Fig. 2b, Table 2) clearly shows that the two subsignals at 39.3° and 39.5° increase at the expense of the peak at 39.8° , suggesting that the incorporation of Sb (and possibly also C) into Pd increases with time on stream. When the catalysts had been pretreated in air instead of He, the downshift of the Pd reflections with increasing time on stream is less pronounced, suggesting that a major part of the metal phase might persist as pure Pd.

Further information about composition, morphology and size of the metal particles has been derived by TEM described below.

3.2.3. Transmission electron microscopy

TEM/EDX results of the catalyst after calcination in air at 600 °C and after 30 h use in the acetoxylation reaction are depicted in Fig. 3. After calcination in air, Pd-containing particles with a size of 5–10 nm are well dispersed over the whole support surface. With regard to the XRD pattern (Fig. 2a), it is most probable that these particles consist of PdO. From EDX alone this conclusion cannot be derived since, due to their small size, the electron beam spot cannot be exclusively focused on a Pd-containing particle alone but hits always a certain area of the support as well. Therefore, radiation emitted from oxygen in PdO and TiO₂ cannot be distinguished. Besides areas with a rather high Pd/Sb ratio, probably arising from the joint detection of small PdO particles and the underlying Sb-containing TiO_2 support (Pd/Sb = 5.4, Fig. 3a), there are Sb-containing support areas without any Pd (Fig. 3a) or with only traces of Pd (Fig. 3b). This suggests that in contrast to Pd which forms a crystalline PdO phase, Sb is highly dispersed on the sup-

Table 2

Peak position, peak area and FWHM derived from XRD patterns of $9Pd12Sb/TiO_2$ samples after different time on stream.

Sample-time on stream	Sub peak position 2 $ heta/^\circ$	Peak area	FWHM
(600-He) fresh	40.01	111.6	0.16
(600-He) – 6 h	39.3	40.2	0.32
	39.5	63.5	0.23
	39.8	221.2	0.31
(600-He) – 32 h	39.3	88.1	0.29
	39.5	102.4	0.30
	39.8	106.3	0.39
(600-air) – 9 h	39.5	92.67	0.34
	39.9	69.68	0.45
	40.2	24.94	0.40
(600-air) – 30 h	39.5	158.2	0.40
	39.9	46.6	0.30
	40.2	29.17	0.30



Fig. 2. XRD patterns of calcined 9Pd12Sb/TiO₂ samples in air, He, 10%H₂/He and respective spent samples after 6–32 h of reaction (left) and deconvolution of the metallic Pd (111) peak into subpeaks (right). Thermal pretreatment was done at 600 °C for 4 h in all cases. 20% Si powder was added to all samples as internal standard: (+ Na₂SO₄, \bigcirc PdO; # Pd, \Rightarrow Pd₈Sb₃, \square NaCl, \star TiO₂).

port. This agrees well with the fact that no crystalline $\mbox{Sb}_2\mbox{O}_3$ has been observed by XRD.

After 30 h use in the catalytic reaction, Pd particles of about 40–100 nm are formed, which are very well crystallized showing a facetted structure (Fig. 3c and d). These particles do contain only some traces of Sb. On the other hand, nearly Pd-free Sb particles were also observed. This shows clearly that the Pd and Sb components remain widely separated in the catalyst.

Very different TEM/EDX results have been obtained from the catalyst pretreated in He at 600 °C. Large Pd particles of up to 2 μ m diameter have been formed during pretreatment in He, leaving a considerable part of the support free of Pd (Fig. 4a and b) but containing Sb as for the air calcined samples. After 32 h on stream in the catalytic reaction, surprisingly, a marked decrease of the particle size down to 40–100 nm was observed, which is equal to the size of the Pd particles formed during time on stream from the air calcined catalyst (compare Figs. 3c and d and 4c and d). However,

in contrast to the latter catalyst, in which the formed Pd particles contain only traces of Sb or Sb particles with traces of Pd (Fig. 3c and d), those in the He-pretreated catalyst are richer in Sb, showing uniform Pd/Sb ratios around 5 (Fig. 4c and d), while the rest of the Sb is spread over the TiO₂ support without forming a separate phase. However, the Sb content detected by EDX on several spots of the support is smaller than observed for the air-calcined catalyst, which might be a consequence of the higher Sb enrichment in the Pd particles. Furthermore, on certain Pd particles which are well separated from the support, traces of oxygen have been detected (Fig. 4c), suggesting a partial oxidation of their surface during time on stream. This has been further explored by XPS described below.

3.2.4. X-ray photoelectron spectroscopy

In Fig. 5 XP spectra of the Pd 3d region are shown for samples after thermal pretreatment at 600 °C in air or He, after stopping the catalytic test in the state of maximum activity (6–9 h on stream)



Fig. 3. Transmission electron micrographs of 9Pd12Sb/TiO₂ samples after 4 h calcination in air at 600 °C (a and b) and after 30 h use in the catalytic reaction (c and d).



Fig. 4. Transmission electron micrographs of 9Pd12Sb/TiO₂ samples after 4 h thermal treatment in He at 600 °C (a and b) and after 32 h use in the catalytic reaction (c and d).



Fig. 5. XP spectra of the Pd 3d peak of $9Pd12Sb/TiO_2$ samples: (a) after 4 h at $600 \degree C$ in He, (b) after 4 h at $600 \degree C$ in air, (c) He-pretreated sample after 6 h on stream, (d) air-pretreated sample after 9 h on stream, (e) He-pretreated sample after 32 h on stream and (f) air-pretreated sample after 30 h on stream.

and after 30-32 h on stream. The Pd $3d_{5/2}$ peak of the catalyst after calcination in air falls at 335.8 eV. This value is in the range of oxidic Pd. This agrees properly with the XRD results in which a crystalline PdO phase has been detected for this catalyst (Fig. 2a). However, this value is considerably lower than the binding energy of 336.5 eV measured for pure PdO (Fig. 5a) [18]. A strong interaction between TiO₂ and the tiny PdO particles can be assumed as reason for the lower binding energy compared to unsupported PdO. Remarkably, the spectrum of the catalysts after pretreatment in He is almost identical to the one after air-calcination (Fig. 5b), although metallic Pd was detected by XRD in this case. This might be due to the formation of surface oxide species on the large Pd particles obtained after the pretreatment in He. It is not likely that these species have been formed by contact with ambient atmosphere at room temperature since similar effects are not observed in other samples discussed below.

In the catalysts removed from the reactor after reaching maximum activity (Fig. 5c and d), two Pd 3d_{5/2} peaks are observed with binding energies of 335.1 eV arising from pure metallic Pd [19] and 336.5 being characteristic for PdO [18]. In the He-pretreated sample, the metallic Pd peak is broader, indicating a higher heterogeneity of the Pd environment and the PdO peak is more pronounced than in the air-calcined sample, in which the majority of Pd on the surface is purely metallic with only a minor contribution of PdO. This could be due to the incorporation of Sb into the Pd phase of the He-pretreated catalyst (as evidenced by TEM and XRD), which might increase the heterogeneity of the Pd environment and obviously stabilizes PdO surface species. Both effects are much less prominent in the XP spectrum of the air-calcined sample (Fig. 5d), in which TEM and XRD suggest that Pd and Sb are spatially widely separated.

After extended time on stream, the resolved PdO peaks disappeared completely in both samples (Fig. 5e and f). However, while an essentially pure Pd surface is evidenced for the air-calcined catalyst, the slight shift of the Pd 3d peak to higher binding energy in the He-pretreated catalysts indicates that the metal surface of the latter remains still partially oxidized. Since both samples have been exposed to ambient atmosphere between removal from the reactor and insertion into the analysis chamber of the XP spectrometer, it is clear that intermediate contact to air does not lead to a reoxidation of metallic Pd in the used samples. The XP spectra of the samples pretreated in H₂/He flow show a Pd peak at a binding energy of 335.6 eV after both the pretreatment and after 8 h on stream, which is similar to the results published in [8] and explained by the formation of a PdSb alloy. No evidence for PdO was found at these samples. In all used catalysts, Sb is present in oxidized form, evidenced by a Sb $3d_{3/2}$ peak with a binding energy of 540 eV, being characteristic for Sb₂O₃ [20].

For exploring changes in the near-surface region in more detail, the metal (Pd, Sb)-to-Ti surface atomic ratios have been calculated based on the areas of the respective Pd3d, Sb3d_{3/2}, Ti2p XPS peaks (see supplementary data, Fig. S2). For the catalyst pretreated in air at 600 °C, the Pd/Ti ratio decreases with time on stream, probably due to Pd particle growth observed with TEM. On the other hand, a slight enrichment of Sb in the surface region was observed. Hence, these opposite trends in the changes of the surface concentration (Fig. S2), suggest a separation of Pd and Sb, which is also supported by TEM results. For the sample pretreated in He, the Sb/Ti ratio increases during the conditioning period while the Pd/Ti ratio remains nearly constant. Upon further time on stream, both ratios decrease in parallel. This suggests spreading of Sb on the surface of the metal particles during conditioning, followed by intermixing of Pd and Sb during further time on stream.

Since coke deposition as a possible reason for catalyst deactivation occurs during time on stream, the C1s region has been analyzed in detail (Fig. 6a). In all samples, a C1s signal at 285 eV is evident, which is typical for C- and H-bound C atoms [21]. The He-pretreated catalyst in the state of its maximum activity shows exclusively this peak. After 32 h on stream, during which a \approx 10% drop in activity was observed (Fig. 1c), an additional C1s signal at 289.5 eV is formed, which is characteristic for C in carboxyl groups [21] (Fig. 6a). In the air-pretreated catalyst, this peak is already present after 9h on stream. A comparison of the relative surface percentage of the types of carbon at spent samples having been pretreated in air or He is shown in Fig. 6b. It is clearly seen that the total amount of surface carbon deposits in the air-calcined catalysts reached its final value already in its state of maximum activity (after 9 h on stream) and then remained constant. In contrast, the total C amount on the surface of the He-pretreated sample increased by a factor of two after 32 h on stream. Interestingly, the total bulk carbon content for the two samples pretreated at 600 °C (Table 1) does not differ much, amounting to 2.2 and 2.4%. Obviously the carbon is a little more enriched on the surface of the catalyst pretreated in He. Nevertheless, its degree of deactivation after 32 h on stream is lower compared to the air-pretreated catalyst (Fig. 1b and c). Probably, carboxylic C deposits as formed in the latter catalysts are stronger deactivating in comparison to C- and H-bound C deposits in the He-pretreated catalyst.

4. Discussion

In this section, an integrated discussion of results of catalytic tests and catalyst characterization is presented to identify reasons of activation and deactivation. First of all, it is evident that the new preparation procedure in which Sb₂O₃ is used as Sb source instead of SbCl₃ without the addition of (NH₄)₂SO₄ as Cl-removing agent, suppresses poisoning of the catalyst surface with sulfide and leads to much more active catalysts than obtained in Ref. [8]. By comparing the catalytic performance of the samples after different thermal

pretreatment procedures (Fig. 1), it is obvious that the latter do not only influence the conditioning time needed to reach maximum activity, but have a major impact also on the deactivation behavior. The most surprising result was the total inactivity of the catalyst pretreated in a flow of 10% H₂/He, over which the toluene conversion was below 1%. As shown by XRD, this pretreatment converts the whole Pd amount into a well defined crystalline Pd₈Sb₃ alloy, which is obviously not active. Since XPS analysis of this sample clearly reveals only one type of Pd before and after the reaction evidenced by a binding energy of 335.6.eV being similar to that found in other PdSb alloys [8], it is very probable that there is no other Pd phase besides the inactive Pd₈Sb₃ phase.

From Fig. 1 it is evident that the catalyst pretreated in air for 2h at 300 °C requires the longest conditioning period. Obviously these conditions are too mild to create Pd-containing particles of suitable size. The conditioning time can be markedly shortened when the pretreatment is done at 600 °C for 4h. Despite the fact that the size and composition of the Pd-containing particles differs markedly, depending on whether the pretreatment was done in air (PdO particles of 5-10 nm) or helium (Pd particles of up to $1 \mu m$), the conditioning time and also the maximum toluene conversion and BA selectivity reached after this time are rather similar (Fig. 1b and c). As we have shown recently [8], there is no doubt that the conditioning time can be shortened by pre-forming Pd particles of suitable size using a tailored thermal pretreatment. However, inspection of Fig. 1 suggests that a rather small size of the starting particles might be sufficient for this effect. Despite the large difference in the starting particle size after air and helium pretreatment, the latter approaches each other during conditioning, which leads to Pd particles of about 40–100 nm independent of the pretreatment atmosphere (Figs. 3 and 4).

The surface area of the TiO_2 support seems to be less important for the catalytic behavior. It decreases to a very different extent during thermal pretreatment at 600 °C in air and He, namely to 115.3 m₂/g and 28.6 m₂/g, respectively (Table 1). Although this may be one reason why the metal particles after treatment in helium are larger in comparison to calcination in air (compare Figs. 3 and 4), this does obviously not influence the catalytic behavior during conditioning which is very similar in both cases (Fig. 1). This suggests that the performance of the catalysts is governed by the nature of the Pd particles and probably also by the surface acidity of the support but not so much by its surface area.

More important, especially for the stability of the catalysts, is obviously the composition of the metal particles, which changes as well during conditioning. XRD and TEM results indicate that the very large pure Pd particles present after pretreatment in helium, restructure during time on stream into smaller ones. Obviously this is caused by migration of Sb species from the support surface into the Pd phase, since the latter contains a considerable percentage of Sb after a certain time on stream, yet without formation of an alloy phase. Sb species exposed on the particle surface are essentially trivalent, as shown by XPS. However, it is probable that in the bulk of the Pd particles they exist in zerovalent form like in PdSb alloys, even though no crystalline alloy is formed in this catalyst.

When the catalyst was pretreated in air, the starting particles are much smaller and consist essentially of PdO. These particles are reduced to metallic Pd and agglomerate during conditioning, yet without remarkable incorporation of Sb. Taking the catalytic test result into account (Fig. 1b and c), it appears that the intermixing of Pd and Sb within the metal particles is essential for ensuring high catalytic performance and long-term stability, as long as the incorporated Sb content remains low enough to prevent alloy formation, which is well known for Pd/Sb ratios of 3:1, 2:1, 1:1 and 1:2 [17].



Fig. 6. (a) XP spectra of the C1s state, (b) relative amount of carboxylic (289.5 eV) and C- and/or H-bound carbon (285 eV) present at the surface of spent 9Pd12Sb/TiO₂ samples pretreated in air or He.

Besides the bulk composition of the metal particles, major differences have also been observed in their surface composition by XPS (Fig. 5). In the state of maximum activity pure metallic Pd⁰ and oxidized PdO species coexist on the surface. This is still the case for the He-pretreated sample after 32 h on stream (Fig. 5e) while the surface of the air-pretreated catalyst lost its oxidized PdO_x after the same time. This goes along with a loss of about 25% in the BA yield, while the latter decreases only by about 10% over the He-pretreated catalyst under the same conditions (Fig. 1b and c). This suggests that the co-existence of both Pd and PdO species is beneficial for high catalytic performance. This has also been proposed for supported Pd catalysts in other oxidation reactions, e.g. the total oxidation of methane [22–25]. It was suggested that the hydrocarbons are adsorbed on the metallic Pd surface sites, while PdO is responsible for their oxidation. Probably, a similar mechanism is valid for the acetoxylation of toluene. Considering the composition of the metal particles, it may be assumed that dissolution of Sb within the Pd particle surface stabilizes oxidized Pd in its vicinity.

Finally we have to consider the impact of the carbon deposits. Although the total amount of surface carbon is lower over the air-pretreated catalyst, its deactivation is more pronounced. XPS revealed that the nature of the carbon deposits after the pre-treatments in air and He at 600 °C is different (Fig. 6). In the air-pretreated catalyst, the relative percentage of carboxylic carbon is higher than after pretreatment in helium. Possibly, product desorption is less easy on the pure Pd⁰ particle surface of the former catalyst, leading to a more pronounced enrichment of carboxylate species, compared to the He-pretreated catalyst.

5. Conclusions

The conditioning time of PdSb/TiO₂ catalysts can be markedly shortened by a thermal pretreatment which is severe enough (600 °C, 4 h) to initiate the pre-formation of Pd-containing particles from the PdCl₂ precursor on the TiO₂ support. However, the performance and particularly the stability of the catalysts depend on the atmosphere of the thermal pretreatment. Reducing atmosphere (10% H₂/He) leads to the formation of completely inactive PdSb alloy particles. Calcination in air creates PdO particles of 5-10 nm, which are reduced to almost pure Pd⁰ with only traces of incorporated Sb during time on stream and which grow to 40-100 nm. In contrast, a helium pretreatment atmosphere forms very large initial Pd⁰ particles (up to 1 μ m) with a partially oxidized surface, that are restructured to smaller ones of 40-100 nm by incorporation of Sb up to a ratio of Pd/Sb \approx 5, yet without formation of stable alloy phases. The surface of these particles contains both, metallic Pd⁰ and PdO species while the surface of the Pd particles of the airpretreated catalyst, though containing some oxidized Pd in the state of highest activity, becomes essentially free of PdO after extended time on stream. In contrast to the air-pretreated catalyst, the one pretreated in helium shows a more stable toluene conversion and BA selectivity. This is most probably due to the co-existence of Pd⁰ and PdO in the latter. This might be favoured by the intermixing of Sb into the Pd particles, which is assumed to stabilize oxidized Pd in its vicinity.

Another reason for the more pronounced deactivation of the airpretreated catalysts results from the nature of the carbon surface deposits. These contain a higher percentage of C=O species which could point to carboxylate-like intermediates that are accumulated on the Pd particle surface, on which PdO with its higher oxidation potential is missing. In summary, it can be stated that the bulk properties of the metal particles formed during pretreatment play an important role for long-time stability by governing the formation of distinct Pd species on the surface during time on stream.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.03.025.

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