Journal of Catalysis 282 (2011) 103–111

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Deactivation and regeneration studies of a PdSb/TiO_2 catalyst used in the gas-phase acetoxylation of toluene

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ARTICLE INFO

Article history:
Received 12 April 2011
Revised 1 June 2011
Accepted 2 June 2011
Available online 5 July 2011

Keywords:
Acetoxylation
Gas-phase reaction
Deactivation
Coking
Regeneration

ABSTRACT

A PdSb/TiO_2 catalyst was subjected to selective gas-phase acetoxylation of toluene (Tol) to benzyl acetate (BA). The catalyst showed low initial activity, which increased with time and displayed maximum activity after 6 h on-stream. The catalyst exhibited stable performance for the next 25 h on-stream and then started to deactivate rapidly. Carbon analysis pointed to coke deposition as a main reason for the loss of catalytic activity. Regeneration at 250 °C could restore the catalyst activity but showed rapid deactivation again in a subsequent run. Regenerative treatment at 300 °C was much more effective not only in restoring the performance but also in maintaining relatively good stability of the catalyst. However, treatment at 350 °C and higher was found to be ineffective in restoring catalytic activity. This surprising behavior of the catalyst was studied in detail with various techniques such as XRD, TEM, and XPS analysis. XRD data give evidence on shifting of Pd reflection to lower 2θ values and the splitting into two parts pointing to different types of Pd species. The surface ratio of Pd^0/PdO of 1 seems to be essential for better performance as revealed by XPS analysis. Surprisingly, this ratio is significantly changed in the deactivated catalyst. Moreover, only metallic Pd species were found on the catalyst surface of this deactivated solid. In addition, regeneration at 300 °C could restore PdO concentration to a greater extent, while the one regenerated at 350 °C could not restore the PdO proportion. This behavior is also believed to be one of the reasons for the unproductive regeneration of deactivated catalyst at 350 °C. Furthermore, Pd^0, PdO, and Sb synergy is needed for stable and high performance of the catalyst.

1. Introduction

The catalytic partial oxidation of various hydrocarbons is one of the most important topics in the field of catalysis due to various challenges involved. The major problem in oxidation reactions is to prevent consecutive oxidation of the desired products into unwanted by-products. This difficulty can be overcome by carrying out controlled oxidation in the presence of efficient catalysts and/or using auxiliary agents. In acetoxylation, oxidation takes place in the presence of acetic acid, and the acetyl group formed prevents the oxygenate from further oxidation. One such good example is the acetoxylation of ethylene [1] in the presence of a Pd catalyst resulting in vinyl acetate, based on an early observation of Moiseev and co-workers [2]; vinyl acetate is one of the big-scale industrial chemicals [3]. A similar reaction with respect to aromatics is the acetoxylation of toluene (Tol) to benzyl acetate (BA) via gas-phase oxidation. BA is naturally found in plants such as jasmine, hyacinth, gardenias, and azaleas. It is used chiefly in the perfume and food industry due to its fruity aroma. It is also used in chemical industry notably as a solvent for cellulose acetate [4]. The global demand for benzyl acetate ranges from 5000 to 10,000 tonnes per annum. In addition, it might serve as an intermediate for the manufacture of benzyl alcohol that is presently obtained by rather harmful chlorination of toluene.

It is widely known that Pd-based catalysts are active and selective for different acetoxylation reactions [5–9], in general. Majority of work in the acetoxylation of toluene to BA is carried out in liquid phase [10–12]. However, there has not been much success in the gas-phase acetoxylation of toluene in the past; very low yields of acetoxylated products were claimed [13–15], and only a maximum yield of BA around 7% could be achieved. Recently, our group [16–20] reported that a titania (anatase)-supported Pd–Sb catalyst gave a high conversion of toluene ($X = 90\%$) with high selectivity of BA ($S = 85\%$). However, such catalyst required a long formation period of around 10 h to exhibit the maximum performance. After acquiring its best activity, the catalyst displayed rapid deactivation after some hours on-stream. Inspired by these limitations of the catalyst, we have recently investigated [21] the effects of calcination atmosphere (air, He, and 10%H_2/He) and temperature (300–600 °C) on the surface properties of the ready-to-use catalyst. It was found that the catalyst treated in helium at 600 °C showed a significant reduction in the formation period from 10 to 6 h. Addi-

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doi:10.1016/j.jcat.2011.06.005

tionally, the catalyst revealed good long-term stability up to 26 h on-stream. However, this catalyst also suffered from deactivation, which presently seems to be inevitable.

The original state of a catalyst changes during deactivation, which could be due to physical and/or chemical changes leading to a loss in activity and/or selectivity [22,23]. Albers et al. [24] have studied the deactivation of Pd catalysts in detail; they identified particle growth, coke deposition transformation, alterations in the support material, and modifications at the Pd surface such as valency changes as main reasons.

In general, coking is among the most common reasons for catalyst deactivation. Many different forms of carbons have been observed in different reactions [25,26]. Some are deposited on the surface of the catalyst, some are transformed from one to another form of carbon, and some are just generated during the reaction and have adverse effect on the catalytic activity. For example, Karge et al. [27] have studied and confirmed the formation of different types of coke on zeolite catalysts. They identified different carbon forms depending upon the temperature of the coke-forming reaction, i.e., at reaction temperature of less than 246 °C and other at temperature higher than 300 °C. These forms could be discriminated by observing different IR bands. It is widely known that Pd catalysts undergo deactivation due to deposited carbon species, either by their deposition on the surface or by their interaction with the surface, e.g., PdC formation. In some cases, the restoration of the catalyst performance is easily and successfully obtained by just burning off such deposits [28]. However, in some deactivated catalysts, regeneration by burning off carbon was not helpful to regain the catalyst initial behavior [29]. In such cases, it cannot just be attributed to the carbon accumulation on the surface, but also to its interaction with active sites of palladium on the surface and the strength of such bonding. Further, some authors have reported [30] that it is difficult to regenerate Pd catalysts because not only the carbon removal is important but also other aspects play a role for restoring activity, e.g., changes in the structure, morphology, and/or valency of the active component.

In the present study, we focus mainly on gaining insights into the deactivation of a Pd–Sb catalyst supported on titania (anatase) and calcined in helium at 600 °C for the acetoxylation of toluene. Moreover, the research was extended further to obtain the best route to regenerate the deactivated catalyst and to restore original activity and selectivity.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Preparation

A 10 wt.% Pd and 16 wt.% Sb on TiO_2 catalyst were prepared in two steps. In the first step, Sb_2O_3 (>99.9% Sigma–Aldrich) powder was suspended in 20 ml distilled water and stirred for 30 min. Then, TiO_2 (anatase, Kronos) was added to Sb_2O_3 slurry and was stirred for 1 h at ambient temperature; 25% ammonia solution was added dropwise to adjust pH = 7. The solution was heated at 70 °C for 1 h, followed by solvent removal in a rotary evaporator. The solid obtained was dried at 120 °C for 16 h and calcined in air at 400 °C for 3 h. In the second step, $PdCl_2$ (>99.9% Alfa) was dissolved in diluted HCl. The solution obtained was cooled to room temperature and 1 N Na_2CO_3 (>99% Alfa) solution was added to adjust the pH = 4. The solid prepared in step 1 was added to the above solution and stirred for 1 h, followed by solvent evaporation in a rotary evaporator. The resulting solid was dried at 120 °C for 16 h and then calcined for 4 h at 600 °C in He flow. Details can be seen elsewhere [21,31].

2.1.2. Characterization

Thermogravimetric analysis and differential scanning calorimetry (TG–DTA) were done with a TGA 92 (Setaram). The heating rate was 10 K/min till 700 °C in air flow.

The elemental composition (Ti, Pd, Sb, and Na) was determined by ICP-OES using a Varian 715-ES ICP-emission spectrometer. The data analysis was performed using the ICP Expert software. Carbon, hydrogen, nitrogen, and sulfur analysis was done using the CHNS microanalysator TruSpec (Leco).

The surface area (BET) and pore size distribution of the catalysts were determined using a Nova 4200e device (Quantachrome Instruments). Before the measurement, the catalyst was evacuated for 2 h at 200 °C to remove physisorbed water.

X-ray diffraction (XRD) powder patterns at ambient conditions were recorded in transmission geometry with Cu Kα 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 *Win Xpow* (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 120 keV using an EM-420T microscope (Philips). Samples were prepared by depositing the catalysts on a copper grid.

X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB 220iXL instrument with Al Kα 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 2p3/2 peak of TiO_2 at 458.8 eV. For the 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.

2.2. Catalyst testing

Heterogeneously catalyzed acetoxylation runs in gas phase were performed in a microcatalytic fixed-bed, vertical, and tubular Hastelloy® C reactor (length 250 mm; i.d. 9.4 mm). The tests were carried out at a reaction temperature of 210 °C and at a reaction pressure of 2 bar. The molar ratio of toluene/acetic acid/oxygen/nitrogen was set to 1:4:3:16 with a gas hourly space velocity (GHSV) of 2688 h^{-1} and a residence time (τ) of 1.34 s. The reaction gases, like O_2 and 5%CH_4/N_2 (used as a diluent gas), were supplied from commercially available compressed gas cylinders and applied without further purification. Methane was used as an internal volume standard. The flow rates of these gases were measured with mass flow controllers. The organic feed mixture (molar ratio of 1:4) of toluene (>99.9%, Roth, Germany) and acetic acid (>99.9%, Walter CMP, Germany) was pumped to the reactor with a HPLC pump (Shimadzu LC 9A). The liquid reactant mixture was vaporized before it entered the reactor in a preheating zone provided on the top of the reactor. Before, the reactor was heated to the desired reaction temperature under inert gas. Afterward, the reactant gases and liquid feed were introduced, and the reaction was carried out. The product stream was analyzed online by gas chromatograph (Shimadzu GC-2010) using a WCOT-fused silica capillary column (60 m, 0.32 mm) and a FID detector with methanizer. Highly purified (>99.99) gases were used for thermal treatment and for catalytic tests.

Calculations of conversion of toluene (X-Tol) and acetic acid (X-AcOH) are based on their molar streams at the inlet and the outlet of the reactor. The yield of formed products (Y_i) and their selectivities (S_i) were calculated from the molar streams too. Besides some carbon oxides from total oxidation, and BA as the main product, minor amounts of benzaldehyde (BAL) were seen. The carbon balance was evaluated from non-converted reactants and yields of identified and calibrated products.

Regeneration of the deactivated catalyst was carried out *in situ* in the used setup at four different temperatures (250, 300, 350, and 400 °C) for 2 h in air.

Several catalyst samples were taken out from the reactor after various reaction stages, deactivation and regeneration. The list of these catalysts studied and their notation used in this paper is given in Table 1.

3. Results and discussion

3.1. Catalyst testing

Fig. 1 clearly demonstrates the catalytic performance of PdSb-f catalyst with time-on-stream (tos). It displays a very low initial activity (X-Tol = ca. 2%), which increased up to ca. 6 h (X-Tol = >50%), remained stable for almost 30 more hours, and then decreased with further increase in reaction time (ca. 18% after 42 h). The yields of BA and BAL as by-products were also observed to change in a similar way as that of conversion of toluene. In addition, CO_2 was also formed to a minor extent. This behavior is due to the fact that catalytic activity is closely connected to Pd particle size and particle composition [17–19]. The catalyst needs a certain amount of time for the growth of Pd particles to a critical size and composition [17]. However, the catalyst showed deactivation above 32 h on-stream. This is due to a predominant coke deposition during the course of the reaction and thereby eventual coverage of the active sites. Table 2 summarizes the amount of carbon deposits at different stages of the reaction. It can be clearly seen that the carbon content increased steadily up to 3 wt.% in the deactivated sample (PdSb-u42).

3.2. Regeneration of 10Pd16Sb/TiO_2 catalyst

As discussed above, a better understanding of deactivation and regeneration processes is essential for improving and optimizing the process conditions. As mentioned above, the major reason for deactivation in the present case seems to be the formation of carbonaceous deposits on the catalyst surface. In addition to carbon deposition, some other modifications of Pd surface such as valency changes or formation of some stable molecular surface species are also speculated.

Table 1
List of catalysts and their denotation used in the acetoxylation of toluene to benzyl acetate and various characterizations.

No.	Catalyst at different stages	Denotation
1	10Pd16Sb/TiO_2-fresh	PdSb-f
2	10Pd16Sb/TiO_2-(used-6 h)	PdSb-u6
3	10Pd16Sb/TiO_2-(used-32 h)	PdSb-u32
4	10Pd16Sb/TiO_2-(used-42 h)	PdSb-u42
5	10Pd16Sb/TiO_2-(used-42 h)-Regeneration@250 °C/2 h/air	PdSb-u42-r250
6	10Pd16Sb/TiO_2-(used-42 h)-Regeneration@300 °C/2 h/air	PdSb-u42-r300
7	10Pd16Sb/TiO_2-(used-42 h)-Regeneration@350 °C/2 h/air	PdSb-u42-r350
8	10Pd16Sb/TiO_2-(used-42 h)-Regeneration@400 °C/2 h/air	PdSb-u42-r400
9	10Pd16Sb/TiO_2-(used-42 h)-Regeneration@300 °C/2 h/air(used-7 h)	PdSb-u42-r300-u7
10	10Pd16Sb/TiO_2-(used-42 h)-Regeneration@350 °C/2 h/air(used-7 h)	PdSb-u42-r350-u7

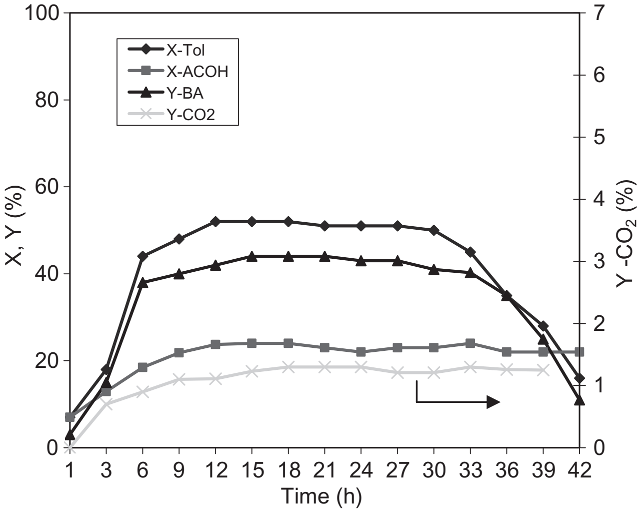

Fig. 1. Catalyst performance of the He calcined 10Pd16Sb/TiO_2 with time-on-stream.

Table 2
Carbon content and BET surface area of the 10Pd16Sb/TiO_2 catalyst at different stages of the reaction.

Catalyst at different stages	C (wt.%)	BET surface area (m^2/g)
PdSb-f	0	28.6
PdSb-u6	0.65	40.6
PdSb-u42	3.0	34.5
PdSb-u42-r300	0.38	31.3
PdSb-u42-r350	0.26	32.2
PdSb-u42-r300-u7	1.78	16.2
PdSb-u42-r350-u7	1.63	18.1

At first, to find out the suitable temperature region for the effective removal of the carbonaceous species, TG–DTA analysis was done until 700 °C in the presence of air. Fig. 2 shows the corresponding plots of the deactivated sample (PdSb-u42). An endothermic broad peak at low temperature (70–100 °C) corresponds to the desorption of physically adsorbed water. Maximum weight loss due to the decomposition of carbon is in the range of 250–400 °C. A weight loss of around 3 wt.% was observed in this temperature range. Hence, temperatures 250, 300, 350, and 400 °C were chosen for the regeneration of the catalyst.

Therefore, the deactivated catalyst was oxidatively treated at four different temperatures with the aim to burn off carbon deposits and also to find out the optimum temperature for effective regeneration. As mentioned earlier, after 42 h on-stream, the conversion of toluene and the yield of BA were decreased from 54% to 18% and 48% to 15%, respectively. Thus, after testing for 42 h, the reaction feed was stopped deliberately and the catalyst was regenerated at the above-mentioned temperatures for 2 h in air. The catalytic performance of the solids after these regenerations is shown in Fig. 3.

For example, PdSb-u42 was regenerated in air at 250 °C for 2 h and then the reaction was continued under identical reaction conditions in order to compare its performance with the fresh catalyst. It is clear from the Fig. 3a that this catalyst (PdSb-u42-r250) could immediately restore its maximum activity. It looks like regeneration was effective at this temperature; however, this sample again undergoes rapid deactivation with time-on-stream, i.e., it is deactivated in this second acetoxylation run at much shorter time-on-stream compared with the first run. This fact suggests that the regeneration temperature (250 °C) was not sufficient enough to effectively burn off coke and restore the activity.

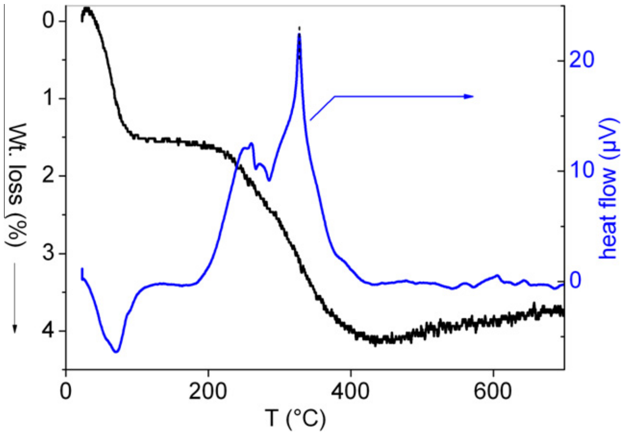

Fig. 2. TG–DTA curves of the deactivated 10Pd16Sb/TiO_2 catalyst (PdSb-u42).

Therefore, another catalyst sample deactivated in an identical manner was treated in a similar way but at higher temperature of 300 °C (PdSb-u42-r300). In this case also, activity and selectivity of the catalyst were completely restored (Fig. 3b). Carbon analysis proved that the deposits were more or less completely burned off (see Table 2). In addition, it has to be noticed that the performance of the sample regenerated at 300 °C was much more effective and stable compared with the catalyst regenerated at 250 °C.

In order to further improve the effectiveness of regeneration compared with those regenerated at 250 and 300 °C, another deactivated sample was treated at 350 °C again for 2 h in air. Surprisingly, it was found that this treatment completely failed to restore activity. The sample showed poor performance (X-Tol ~18%, Y-BA ~15%) as depicted in Fig. 3c. To confirm this result further, we treated another deactivated catalyst even at higher temperature of 400 °C, which led to poor performance as well (Fig. 3d).

From the above observations, it can be concluded that catalyst deactivation is reversible only if the catalyst is treated at the temperatures of 250 and 300 °C. Obviously, higher temperature of 350 °C and above is not suitable to recover the catalyst performance. The regeneration temperature of 250 °C can restore the activity but not for a prolonged period of time. Among all the four temperatures investigated, it is clear that 300 °C regeneration temperature is most effective in restoring activity and also giving stable performance in a further catalytic run.

3.3. Characterization of fresh, deactivated, and regenerated 10Pd16Sb/TiO_2 catalysts

3.3.1. Carbon analysis

After acetoxylation runs on the catalyst PdSb-f, we observed that the catalyst changed its color from brown to black, indicating that the catalyst was obviously covered by coke. Therefore, carbon content measurements were taken, and the relationship between catalyst performance and the amount of coke present at different stages of the reaction is shown in Fig. 4. It can be noticed that during the formation period of 6 h (i.e., up to maximum activity), carbon already starts to deposit (about 0.6 wt.%, see Table 2). However, such small amount of carbon in this stage is not large enough to block the active sites and to decrease the activity. The carbon content is progressively increased further to about 2 wt.% after 32 h on-stream, but still the activity is maintained. Interestingly,

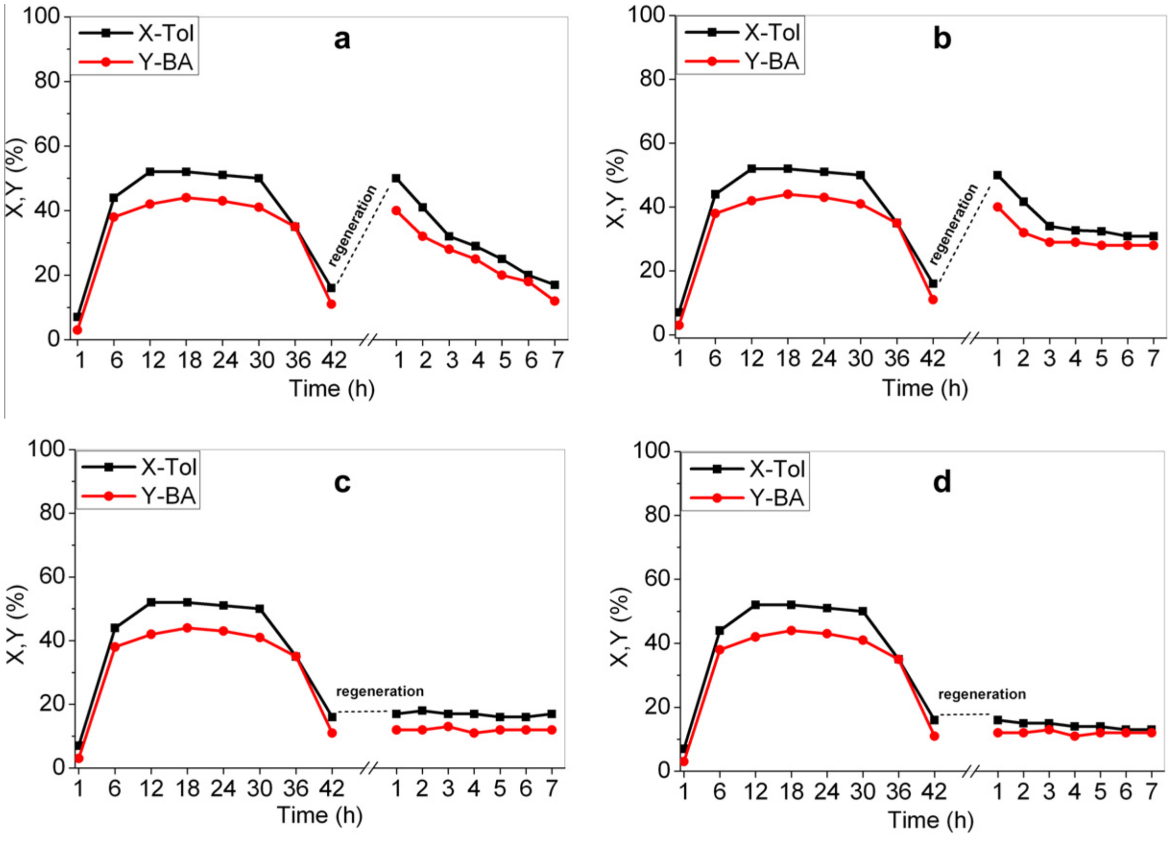

Fig. 3. Catalyst performance and regeneration of the 10Pd16Sb/TiO_2 at different temperatures for 2 h in air: (a) 250 °C, (b) 300 °C, (c) 350 °C, and (d) 400 °C.

about 2 wt.% coke has only a marginal influence on the performance. However, when the coke amounts further increase beyond 2%, the catalyst undeniably undergoes deactivation. As a result, a sharp decrease in the conversion of toluene and yield of BA was observed.

Carbon content was also determined for the four samples collected after regeneration at 250, 300, 350, and 400 °C. Only the data of the samples regenerated at 300 °C (PdSb-u42-r300) and 350 °C (PdSb-u42-r350) are given (see Table 2) because carbon contents of the other samples are quite similar. Obviously, carbon deposits can be removed from the catalyst at both the temperatures by more than 80–90%. In contrast, XPS reveals that there is more surface carbon in the sample regenerated at 350 °C than one at 300 °C. This seems to be the reason for ineffective regeneration of deactivated solid at 350 °C. Then, second acetoxylation runs were also carried out on the regenerated samples and the carbon content was analyzed again, which was found to increase considerably in 6–7 h on-stream. The poor performance of the catalysts regenerated at 350 °C and higher suggests that certain structural changes or some other alterations such as valency changes are probably taking place during higher temperature treatment.

3.3.2. BET surface areas and pore size distribution

The BET surface areas of fresh (PdSb-f), maximum active (PdSb-u6), deactivated (PdSb-u42), regenerated at 300 °C (PdSb-u42-r300) and 350 °C (PdSb-u42-r350), and used (second reaction run) samples (PdSb-u42-r300-u7 and PdSb-u42-r350-u7) are presented in Table 2. A significant increase was observed from fresh to maximum active catalyst, i.e., from 28.6 to 40.6 m^2/g, respectively. The surface area also changed to some extent during the course of the reaction and even after regeneration, which remained in the range of 40–32 m^2/g. However, a dramatic decrease in surface area from nearly 32 m^2/g to 18–16 m^2/g was observed in the solids studied after the second reaction run. This suggests that coking of catalysts after regeneration step is much easier and/or other structural alterations took place.

The pore size distribution of the deactivated, regenerated, and used samples in the second reaction run after regeneration is quite similar to that of the fresh catalyst (Fig. 5). However, the sample regenerated at 350 °C shows a significant increase in pore volume; it is nearly doubled for larger pores compared with the sample regenerated at 300 °C. This might be a possible reason for the loss in surface area.

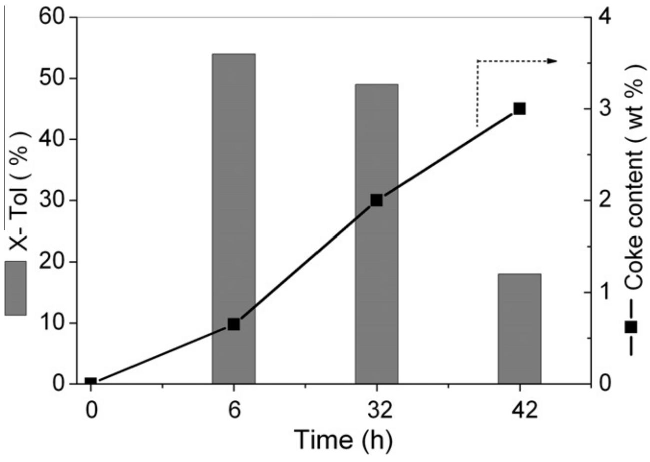

Fig. 4. Correlation between the catalyst performance and the coke formation with time-on-stream.

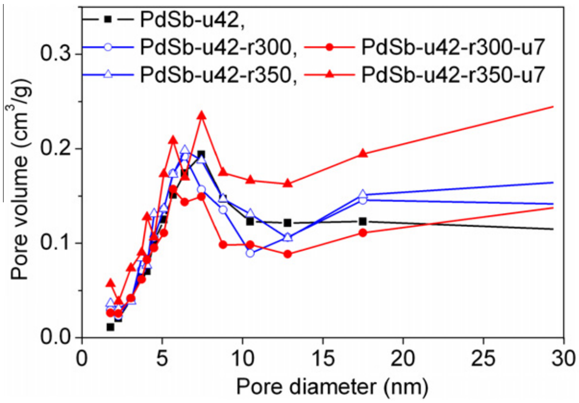

Fig. 5. Pore size distribution of 10Pd16Sb/TiO_2 samples at different stages of reaction.

3.3.3. X-ray diffraction

XRD patterns of the fresh (PdSb-f), maximum active (PdSb-u6), and deactivated (PdSb-u42) catalysts along with the solids regenerated at 300 °C (PdSb-u42-r300) and 350 °C (PdSb-u42-r350) are shown in Fig. 6a. The XRD patterns of all samples show reflections of the anatase support, NaCl (which is formed by Na_2CO_3 and $PdCl_2$ used during the preparation). In addition, a shift and a splitting of metallic Pd reflections were observed compared with those in the fresh catalyst during the course of reaction, which are shown in Fig. 6b. It is known that pure metallic Pd reflections (Pd(1 1 1)) appear at $2\theta = 40.01°$ [PDF. No. 88-233] and are related to the cubic structure with cell parameter of 3.905 Å. But in all diffractograms except for that of the fresh sample, this peak is shifted to lower 2θ values. In addition, XRD reflections of PdSb-u6 and the regenerated samples PdSb-u42-r300 and PdSb-u42-r350 show a splitting of the Pd peak (see Fig. 6b). Such shift and splitting of the Pd peak are due to the incorporation or formation of solid solution between Pd and Sb or C, which was, however, explained earlier [21]. It is known that such incorporated carbon can be removed with heating in air below 300 °C [32]. The regenerated samples showed lattice expansion with two separate reflections at $2\theta = 39.8$ and 39.5°. This clearly points to the incorporation of Sb in the Pd lattice. It must be noted that the diffractograms of the most active (PdSb-u6) and the regenerated samples are very similar. In contrast, the completely deactivated PdSb-u42 showed a broad asymmetric reflection below $2\theta = 40°$. A deconvolution of this broad peak is not possible due to the presence of various Pd species. The differences between the Pd reflections in the spent sample (PdSb-u42) and both the regenerated samples are mainly caused by the removal of carbon during the regeneration. However, XRD provides no hint for the poor performance of the samples regenerated at higher temperature (350 and 400 °C) in the subsequent catalytic run. This surprising result is clearly explained by other techniques as described below.

Fig. 7a and b displays the diffractograms of the catalysts used in a second acetoxylation run after regeneration at 300 and 350 °C (PdSb-u42-r300-u7 and PdSb-u42-r350-u7). From these reflections, it can be seen that the shifted splitting of the Pd peak at 40.01° is significantly observed only in the sample treated at 300 °C for 2 h in air, whereas in the case of 350 °C, additional reflections at $2\theta = 40.2°$ and 40.6° are related to a definite intermetallic compound (i.e., $Pd_{20}Sb_7$ phase [PDF. No. 31-102]) appeared after second run. It is known that the formation of this alloy is detrimental to the activity [21]. As such, from the above observations, it can be stated that bulk compositions are not determining the performance of the catalyst. Near-surface region properties

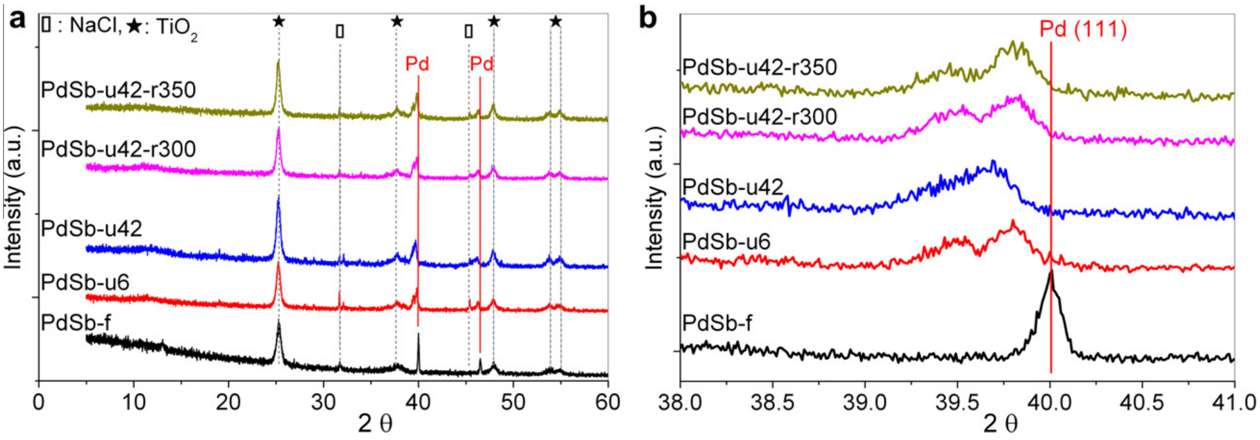

Fig. 6. (a) XRD patterns of samples of fresh (PdSb-f), maximum active (PdSb-u6), deactivated (PdSb-u42), and regenerated 10Pd16Sb/TiO_2 catalysts (PdSb-u42-r300 and PdSb-u42-r350). (b) XRD patterns in the 2θ range of the Pd(1 1 1) reflection (38–41°).

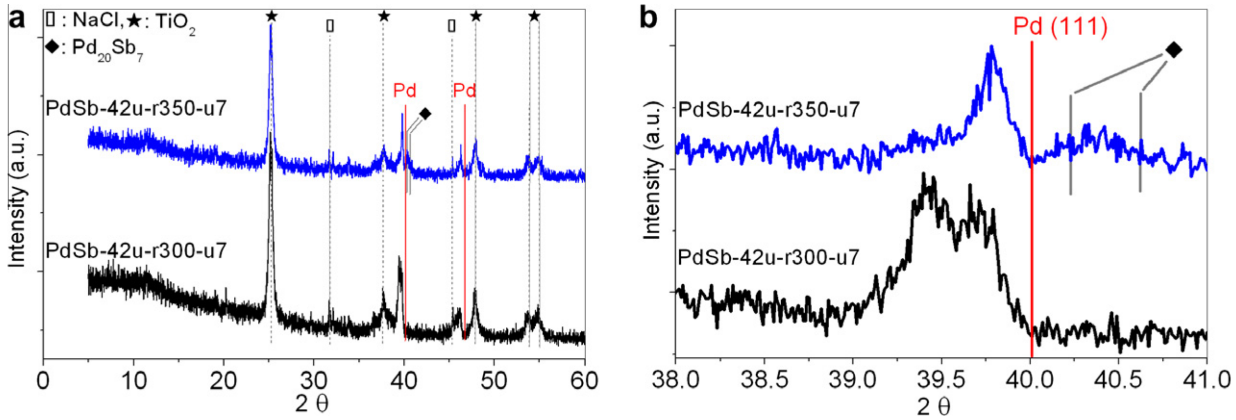

Fig. 7. (a) XRD patterns of 10Pd16Sb/TiO_2 samples used in a second reaction run after regeneration at 300 and 350 °C (PdSb-u42-r300-u7 and PdSb-u42-r350-u7, respectively). (b) XRD patterns in the 2θ-range of the Pd(1 1 1) reflection (38–41°).

probably play an important role and are monitoring the activity of the catalysts.

3.3.4. Transmission electron microscopy

Fig. 8a–d shows electron micrographs of deactivated (PdSb-u42) and regenerated catalyst samples. The deactivated samples display spherical-shaped particles with the size varying in the range of 50–100 nm. TEM images of the samples regenerated at different temperatures also reveal that the shape and size of most of the particles remain unchanged throughout irrespective of thermal treatment given, i.e., no effect on the size and morphology was observed. However, restructuring of particle with tri or hexagonal array was observed only in the sample after regeneration at 400 °C.

From previous studies [19], it is known that one of the reasons for high catalytic performance is an optimum particle size of Pd. It was found recently [17,33] that it needs to attain some critical size (50–100 nm) to show the best performance with good long-term stability. However, in the present series, all regenerated catalysts have almost the same particle size as that of the catalyst during the reaction (50–100 nm). These observations suggest that the size of the particles cannot be the reason for the observed differences in their behavior after regenerations. Even regeneration treatments of 300–400 °C for 2 h in air revealed no influence on the particle size. Therefore, we can say that the poor performance of the catalysts regenerated at higher temperature has nothing to do with the particle size of the Pd of the catalyst. Surface properties probably play a more important role in determining the fate of the regenerated catalysts in the acetoxylation reaction.

3.3.5. X-ray photoelectron spectroscopy

The XP spectra of the fresh sample, after 6 h on-stream (PdSb-u6), the deactivated sample (PdSb-u42), and two regenerated samples (i.e., one at 300 °C (PdSb-u42-r300) and the other at 350 °C (PdSb-u42-r350)) are displayed in Fig. 9. The Pd binding energy of the fresh sample was found to be 335.8 eV. This value corresponds to that of oxidic Pd [34]. During the reaction, generation of other Pd species was also observed (around 335 eV), which corresponds to metallic Pd [35] and PdO (336.5–337.5 eV) [34] Both Pd^0 and PdO phases were present until the catalyst showed stable performance from 6 h up to 32 h on-stream (X-Tol = 54% and Y-BA = 48%), while the PdO peak vanished in the deactivated catalyst (where X-Tol = 18%, Y-BA = 15%; PdSb-u42).

In addition, spectra of catalysts used in a second reaction run for additional 7 h after regeneration at above two temperatures (PdSb-u42-r300-u7 and PdSb-u42-r350-u7) are shown. After 6 h on-stream, in which the catalyst reaches its maximum performance, peaks corresponding to both the metallic Pd^0 and PdO were observed. This means that during the first few hours of reaction, reduction is occurring to a certain extent. As the reaction proceeds, a further gradual reduction of PdO species was seen. After 42 h on-stream, the catalyst is deactivated and PdO species completely vanished from the surface, while only the metallic Pd^0 species remained. From these observations, it can be concluded that the

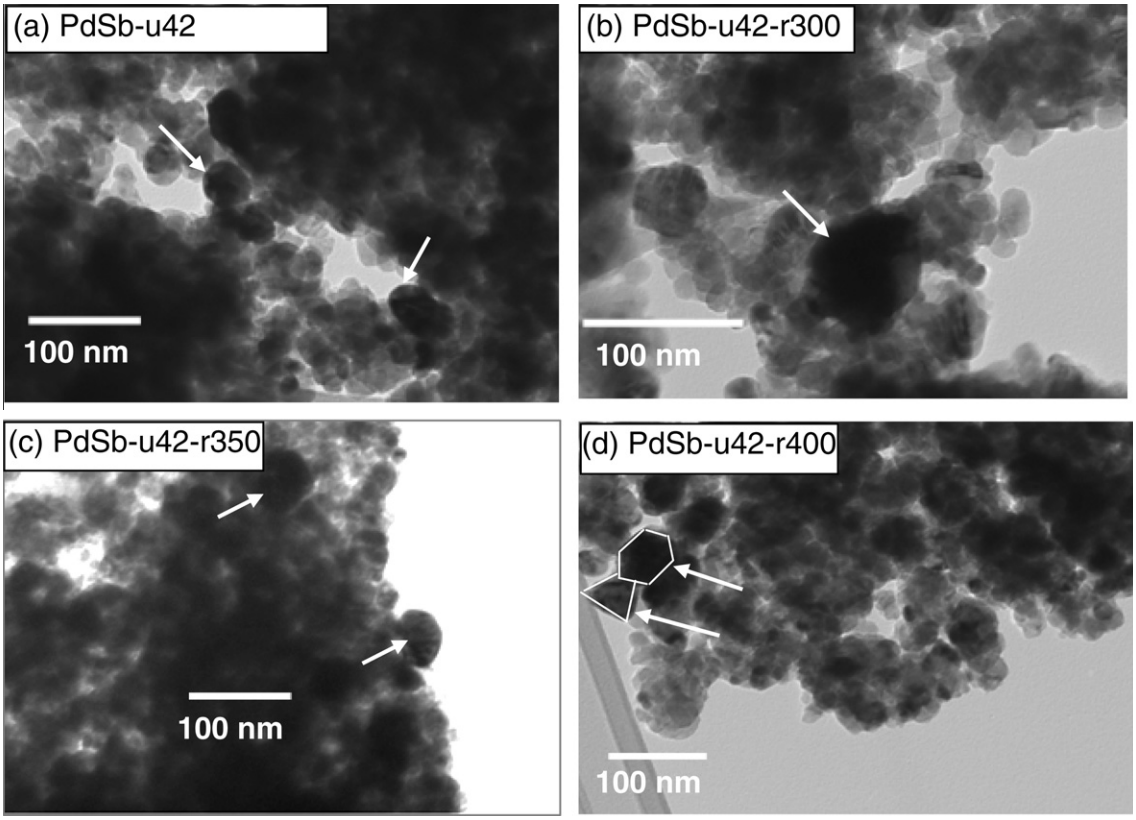

Fig. 8. Transmission electron micrographs of 10Pd16Sb/TiO$_2$ samples after (a) deactivation (PdSb-u42) and regeneration at (b) 300 °C (PdSb-u42-r300), (c) 350 °C (PdSb-u42-r350), and (d) 400 °C (PdSb-u42-r400) for 2 h in air.

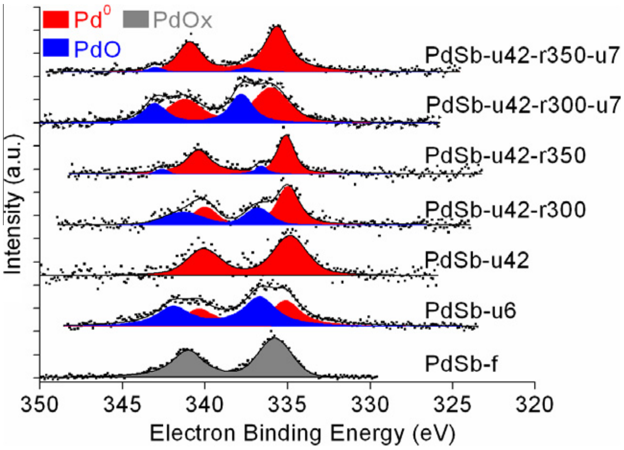

Fig. 9. XP spectra of the Pd 3d peak of 10Pd16Sb/TiO$_2$ samples at different stages of the reaction (PdSb-u6, PdSb-u42, PdSb-u42-r300, and PdSb-u42-r350) and these samples used in a second reaction run after regeneration PdSb-u42-r300-u7 and PdSb-u42-r350-u7).

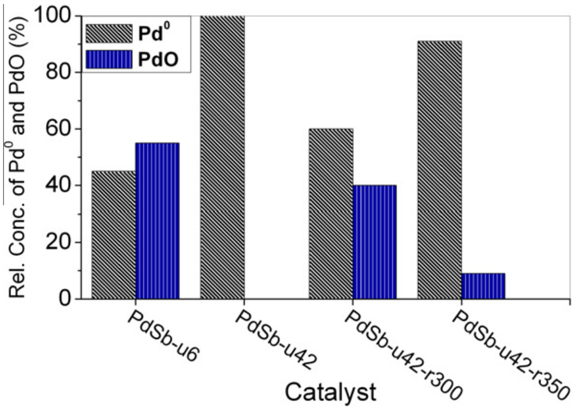

Fig. 10. Relative surface concentration of Pd^0 and PdO in 10Pd16Sb/TiO$_2$ samples at different stages of reaction (PdSb-u6, PdSb-u42, PdSb-u42-r300, and PdSb-u42-r350) analyzed by XPS.

presence of both the Pd^0 and PdO species on the surface is vital for the best performance of the catalyst. Especially for the spent catalysts, certain changes in the peak shape is noticed, i.e., significant broader peaks were observed than for the regenerated samples, indicating a higher chemical heterogeneity in the surrounding of the Pd atoms.

XP spectra of samples after regeneration at 300 and 350 °C for 2 h in air (PdSb-u42-r300 and PdSb-u42-r350) again showed PdO species, which were lost in the deactivated sample. However, the spectrum of the catalyst regenerated at 350 °C shows that this treatment is not suitable to regenerate the initial concentration of PdO on the surface. Additionally, we also estimated the surface concentration of Pd^0 and PdO species in these samples (Fig. 10), which again gave clear hints that the presence of PdO in addition to coke removal is essential to get back good performance. It is clear from this estimation that the sample regenerated at 350 °C only shows a Pd^0/PdO surface ratio of 9:1, while the sample regenerated at 300 °C reveals a ratio of 6:4. On the other hand, the maximum active sample (PdSb-u6) shows a ratio of 4.5:5.5. It is very interesting to note that even though some PdO species were found on the surface of the catalyst treated at 350 °C, the catalyst activity did not return to its initial level. This suggests that not just the

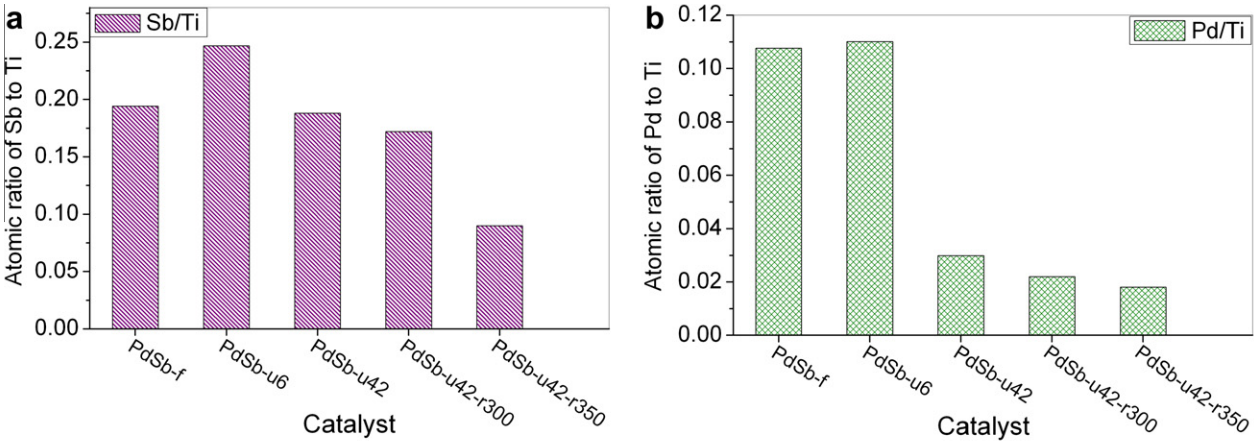

Fig. 11. (a) Surface Sb/Ti atomic ratio in 10Pd16Sb/TiO_2 samples at different stages of the reaction (PdSb-f, PdSb-u6, PdSb-u42, PdSb-u42-r300, and PdSb-u42-r350) analyzed by XPS. (b) Surface Pd/Ti atomic ratio in 10Pd16Sb/TiO_2 samples at different stages of the reaction (PdSb-f, PdSb-u6, PdSb-u42, PdSb-u42-r300, and PdSb-u42-r350) analyzed by XPS. Surface atomic ratios were calculated from the areas of the XPS Sb3$d_{3/2}$, Pd3d, and Ti2p peaks.

existence of PdO and Pd^0 species but their optimum ratio seems to be essential for the high performance of the catalyst.

The C1s spectra of all spent and regenerated catalysts consist mainly of two peaks at 284.8 eV and 289.5 eV. The former one is originated from carbon atoms bonded to other C atoms or H atoms, while the latter one is correlated with carboxylic groups. As expected, the highest carbon amount was found for the deactivated sample after 42 h on-stream. The regeneration at 300 °C has shown a significant decrease in the carbon amount in the near-surface region, but surprisingly, it is not that effective for the one regenerated at 350 °C in air. Possible explanation for this unexpected behavior at such higher temperature treatment is the formation of stable carbon surface species (e.g., Pd carbides) or a possible transformation of Pd surface structures toward those stabilizing adsorbed carbon. This high amount of deposited carbon explains the low activity of this sample regenerated at 350 °C.

Sb concentration on the surface of fresh (PdSb-f), maximum active (PdSb-u6), deactivated (PdSb-u42), and regenerated solids (PdSb-u42-r300 and PdSb-u42-r350) were also studied using XPS. The spectra revealed that Sb is present in oxidized form, evidenced by a Sb 3$d_{3/2}$ peak with a binding energy of 540 eV, being characteristic for Sb_2O_3 [36]. From the surface Sb/Ti atomic ratios (Fig. 11a), it is evident that the maximum active sample contains the highest Sb proportion at the surface compared with deactivated and regenerated samples. Interestingly, in the sample regenerated at 350 °C, the Sb concentration in the near-surface region could not be restored considerably. In other words, the amount of Sb regained after regeneration at 350 °C is only about 40% of the surface Sb present in the sample regenerated at 300 °C. Probably, this deficit of surface Sb would be related to the small proportion of PdO in the sample regenerated at 350 °C (PdSb-u42-r350).

A similar trend was also observed in the case of Pd/Ti surface ratio (Fig. 11b). The surface Pd amount was found to be dramatically reduced in the deactivated catalyst (PdSb-u42) compared with the one at maximum activity (PdSb-u6). This loss of surface Pd could not be restored adequately after regeneration. This might be a further reason for faster deactivation and surface area loss after second catalytic run. Here, one should note that elemental analysis by ICP-OES of the spent catalysts at different stages, deactivated and regenerated catalyst did not show any loss of Pd or Sb from the catalyst. Therefore, the possibility of leaching of Pd or Sb from the catalyst can be ruled out. In summary, the catalytic performance is related to the surface concentration of Pd and Sb and the amount of deposited coke. On the whole, it can be said the optimum combination of these three parameters is essential for maintaining the good and stable performance of the catalyst.

4. Conclusions

10Pd16Sb/TiO_2 catalyst was used for the gas-phase acetoxylation of toluene showing best performance of X-Tol = 54% and Y-BA = 48% after a formation period of 6 h. Despite this, after nearly 30 h, on-stream catalyst loses performance and reveals typical deactivation behavior. Regeneration was carried out in air for 2 h at four different temperatures (250–400 °C). Treatment at 250 and 300 °C was found to be suitable to regain catalyst performance. Higher temperature treatment (350 and 400 °C) was not suitable for regeneration, and hence, the catalyst did not regain the activity lost during the deactivation. Carbon analysis yielded a more or less effective removal of coke deposits after regeneration. However, the samples regenerated at higher temperatures remained inactive in a second catalytic run. XRD patterns revealed a splitting and shifting of Pd(1 1 1) to lower 2θ values. This behavior seems to be caused by the interaction of Pd with surrounding Sb and/or Ti of the carrier. However, no real reason for the regeneration properties can be seen. TEM studies revealed that there is no change in Pd particle size after reaching the optimum of 50–100 nm during formation period. Detailed XPS characterizations showed that an optimum amount of PdO and Pd^0 on the surface is necessary for the better performance of the catalyst. The PdO deficit in the sample regenerated at 350 °C seems to be mainly responsible for the poor performance after regeneration. This deficit is due to the migration of Pd to deeper layers as discovered by XPS; in addition, the surface Sb proportion also seems to be lowered in those regenerated catalysts. Thus, the existence of Pd^0, PdO, and Sb synergy on the catalyst surface is needed to maintain a stable and high performance of the catalyst.

Acknowledgments

The authors like to thank Leibniz-Institut für Katalyse e.V. and Deutsche Forschungsgemeinschaft (Grant No. BR1380/13-2) for the financial support. Authors also thank Mr. Samudra Sengupta, Pennsylvania State University, USA, for carrying out TEM analysis and our analytical staff, especially Dr. M. Schneider, at LIKAT for CHN and XRD analyses.

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