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Effect of Sb loading on Pd nanoparticles and its influence on the catalytic performance of Sb–Pd/TiO$_2$ solids for acetoxylation of toluene

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Abstract

Gas-phase acetoxylation is a green technology for the direct synthesis of aromatic and heteroaromatic acetates in a single step from their corresponding alkyl aromatics and heteroaromatics. Moreover, aromatic as well as heteroaromatic alcohols are easily accessible by subsequent hydrolysis. We observed in an earlier study that the addition of Sb to Pd catalysts is responsible for enhancing the yield of benzyl acetate in the acetoxylation of toluene. In the present contribution, we report for the first time the dependence of Pd particle size on Sb loading and its influence on catalytic performance. Furthermore, to gain deeper insight into the role of Sb, a series of Sb–Pd/TiO$_2$ catalysts with different Sb loadings (4–20 wt%) was prepared with constant Pd proportion (10 wt%), characterised by N$_2$ adsorption, XRD, TEM, and XPS and tested at 210 °C and 2 bar. BET surface areas and pore volumes were observed to decrease considerably, from 96 to 39 m^2/g and 0.164 to 0.058 cm^3/g with increasing Sb loading from 4 to 20 wt%. XPS results showed that the presence of Sb influences both the valence state of Pd and the amount of coke deposition during the reaction. TEM analysis revealed that Sb is found to be always present together with titania (support). No separated free Sb particles and no intermetallic formation between Sb and Pd is seen even with higher Sb loading (20 wt%). On the other hand, free Pd particles with spherical morphology are clearly seen. The initial size of Pd particles in the fresh catalysts is approximately 1–10 nm depending on the Sb loading. However, the samples used exhibited much larger Pd particles (up to 90–100 nm), indicating significant growth during the course of the reaction. The presence of Sb revealed a significant influence on increasing the size of Pd nanoparticles, which in turn showed an appreciable influence on catalytic performance. The activity of the catalysts is found to increase continuously with increasing Sb loading up to 8 wt% and then decrease slightly with further increase. The catalytic activity is observed to change more or less in a similar fashion as that of changes in Pd particle size of the fresh catalysts (i.e., enhanced catalytic performance accompanied by the formation of larger Pd particles). The catalyst with a Sb loading of 8 wt% exhibited the best performance among all other solids of this series, giving 68% conversion of toluene and 85% selectivity of benzyl acetate. Interestingly, all fresh catalysts displayed very low initial activity (X-Tol = <5%), which increased with time until steady-state conditions were attained, remained stable for few more hours, and then declined with further increases in reaction time. The increased catalytic activity is attributed to increased Pd particle size, whereas the decreased activity is due to coke deposits, as evidenced from TEM and carbon analyses. But these solids can be readily regenerated in air to restore their maximum activity. The correlation between the C/Pd ratio obtained by XPS and the catalytic results suggests that the carbon–palladium interaction is the main reason for catalyst deactivation and depends on the size and shape of the Pd particles. An attempt has been made through the current study to describe the present state of understanding of the potential effects on catalytic performance induced by varying the Sb loading.

Keywords: Gas-phase acetoxylation; Toluene; XRD; TEM; XPS; Sb–Pd/TiO$_2$ catalysts; Particle size effects; Sb loading

1. Introduction

Multicomponent systems have long been considered interesting catalytic materials from both academic and industrial standpoints [1–5]. In recent years, numerous studies have addressed supported catalysts with two or more metallic components [6,7]. Furthermore, the ever-growing number of multi-

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component systems in industry has led to better catalyst performance; however, there remains a need for better understanding of these catalysts' structural and electronic properties [8]. The advantages include improved activity and selectivity, increased catalyst lifetime, improved deactivation resistance, and others. In view of such beneficial effects, the catalysts with two or three metallic components are also being used for different acetoxylation reactions in general [9,10] and toluene acetoxylation in particular [11–13]. Nonetheless, for most such systems, the precise role of a second and/or third metal on improving the performance remains a matter of debate.

Acetoxylation is a simple method for producing various industrially useful esters in a single-step reaction from their corresponding olefins or alkyl aromatics and appropriate carboxylic acids. Acetoxylation of simple olefins such as ethylene [14,15], propylene [16,17], and butadiene [5,10,18] to their corresponding esters is widely used in industry. However, the extension of this work from simple olefins to aromatics is still in a developmental stage, especially using gas-phase conditions. Gas-phase acetoxylation of toluene to benzyl acetate (BA) is an attractive and industrially important reaction because the target product (i.e., BA) is applied in food, chemical, and perfumery industries. Especially for the production of benzyl alcohol, which can be readily obtained by hydrolysis of BA, the present route is an environmentally acceptable alternative compared with the existing methods using chlorine chemistry.

It is clear from the state of the art [19–24] that Pd-based catalysts are widely used for the acetoxylation of toluene. However, no acceptable success has been achieved so far in terms of obtaining higher yields of BA with longer catalyst life. In the direction of developing novel Pd-based acetoxylation catalysts, our previous investigations focused mainly on the influence of Pd loading [25,26], different promoters [27], prevention of catalyst deactivation by adding Bi to the Pd–Sb system [28], and understanding the deactivation phenomenon [29]. The basis for the present investigation is our earlier observation on the catalytic performance of monometallic anatase-supported catalysts, such as Pd/TiO_2 and Sb/TiO_2 solids. These samples displayed very poor performance, giving just ca. 2% toluene conversion. Separate experiments [26] also proved the unselective nature of monometallic catalysts, particularly Pd/TiO_2, giving mainly total oxidation products (CO_x up to 50%) due to the oxidative decomposition of acetic acid. However, the combination of both Sb and Pd (i.e., Sb–Pd/TiO_2) not only suppressed the oxidative decomposition of acetic acid, but also notably improved the catalytic performance due to synergistic effects between Sb and Pd [26].

In addition, relatively high Pd loadings (10–20 wt%) were found to be optimum for obtaining better catalytic performance. Unfortunately, these catalysts deactivate with time on stream (i.e., mostly a few hours after attaining steady-state conditions). The loss of Pd and Sb in the near-surface region caused by coke deposition was assumed to be the main reason for such deactivation. Further studies showed that the addition of Bi prevents catalyst deactivation [29], influences the redox properties of Pd, and stabilises PdO_x surface species. In addition, the so-called "Pd(δ^-)," an electronic state with an electron binding energy lower than that of metallic Pd (BE. of Pd = 335.1 eV) was not formed in presence of Bi. The existence of this Pd(δ^-) state was correlated with catalyst deactivation. Furthermore, larger Pd particles were also found to be favourable for obtaining better performance. The larger Pd particles (up to 100 nm) are necessary for the reaction to take place more efficiently. In addition, no hints for intermixing of Pd and Sb leading to the formation of either intermetallics or alloys were found in these investigations. At this early stage of study, the role of Sb on enhancing the catalytic performance of monometallic Pd catalysts remains somewhat unclear.

Bearing all of these factors in mind, the present study is aimed at investigating the influence of Sb loading over a wide range to gain new insights into the role of Sb used as a co-component. Special attention was also given to evaluate the influence of Sb on various distinct features (i.e., particle size and growth during the course of the reaction, redox properties of Pd, and coke deposition) which were found to be critical for tuning the catalyst performance.

2. Experimental

2.1. Catalyst preparation

Different Sb–Pd/TiO_2 catalysts with varying Sb loadings were prepared by a wet-impregnation technique. Preparation of these catalysts involved mainly two steps:

- Step 1. Commercial TiO_2 anatase (BET-SA: 315 m^2/g, Kronos, Germany) was first impregnated with an aqueous solution of $SbCl_3$ (99.8%, Alfa Produkte, Karlsruhe, Germany) in desired amounts and soaked for 1 h at room temperature. Then the slurry was filtered and dried on a rota-vapour to remove excess water. The resulting solid mass was dried in an oven at 120 °C for 16 h, followed by calcination at 400 °C for 3 h in air (50 ml/min).
- Step 2. The Sb-impregnated TiO_2 samples obtained from step 1 were further impregnated with the acidified aqueous solution of $PdCl_2$ to get 10 wt% Pd in the final catalyst. The excess solvent was then removed by rota-vapour, and the sample was dried in an oven at 120 °C for 16 h. The Pd content was kept constant at 10 wt% in the catalysts, whereas the Sb loading was varied between 4 and 20 wt%. The detailed procedure for catalyst preparation has been reported elsewhere [30].

2.2. Catalyst characterisation

BET surface areas of the catalysts were determined on a Gemini III-2375 (Micromeritics) instrument by N_2 physisorption at −196 °C. Before the surface area measurements, the known amount of catalyst was evacuated at 150 °C for 2 h to remove physically adsorbed water.

XRD patterns were obtained on a X-ray diffractometer STADI-P (Stoe) using Ni-filtered CuK_α radiation ($\lambda = 1.5418$ Å). The powder samples were placed on a quartz monocrystal sample holder (Stoe). The crystalline phases were identified by referring to ASTM data files.

Samples for TEM were prepared by depositing the catalyst on a copper grid (300 mesh) coated with carbon film (Lacey). The TEM analysis was carried out using CM-20 microscope (Philips) at 200 kV with EDAX PV9900.

The X-ray photoelectron spectroscopic (XPS) measurements were done with an ESCALAB 220iXL. AlK_α radiation was used to obtain the XP spectra. The spectra were referred to the Ti $2p_{3/2}$ peak of TiO_2 at 458.8 eV. The binding energy scale was calibrated with pure and clean Cu, Ag, and Au samples. For quantitative analysis after Shirley background subtraction, the peaks were fitted with Gaussian–Lorentz curves. The peak areas thus obtained were divided by the element-specific Scofield factor and the analyser-specific transmission function to get the composition in the near-surface region.

2.3. Activity measurements

Acetoxylation runs were performed in a fixed-bed microcatalytic stainless steel reactor. One ml of catalyst particles (0.425–0.6 mm size) was loaded into the reactor, and the reaction was performed at 210 °C and 2 bar in general. The reaction feed consisted of air (as a source of oxygen) and an additional inert gas (argon) to maintain constant space velocity as well as toluene and acetic acid. The compressed gases, including argon (99.99%) and synthetic air (20.5% O_2 in nitrogen), were supplied from commercially available gas cylinders and used without further purification. The flow rates of these gases were measured using mass flow controllers. The catalyst was activated in airflow (27 ml/min) at 300 °C for 2 h before the activity measurements. The premixed organic feed of toluene and acetic acid at a molar ratio of 1:4 was pumped to the reactor using a HPLC pump. The product stream was analysed on-line by a gas chromatograph (HP-5890) equipped with a flame ionisation detector module using a HP-5 capillary column (50 m × 0.32 mm). The column outlet was connected to a methaniser (30 wt% Ni/SiO_2 catalyst), which converted all of the carbon-containing products, including CO and CO_2, into methane. This enabled reliable and simple quantitative analysis of the products. More experimental details on catalytic testing and product analyses have been given elsewhere [26].

3. Results and discussion

3.1. BET surface areas and pore volumes

BET surface areas and pore volumes of the various Sb–Pd/TiO_2 catalysts are presented in Table 1. It is clear from the table that the surface areas and pore volumes decreased from 96 to 39 m^2/g and 0.164 to 0.058 cm^3/g with increasing Sb loading from 4 to 20 wt%. Similar such tendency of decreasing surface areas and pore volumes were also observed from previous studies with increased Pd loading from 0.5 to 20 wt% [26].

Table 1

BET surface areas and pore volumes of Sb–Pd/TiO_2 catalysts with different Sb loadings

Sb loading (wt%)	BET-SA (m^2/g)	Pore volume (cm^3/g)
4	96	0.164
6	82	0.142
8	78	0.127
12	72	0.123
16	46	0.071
20	39	0.058

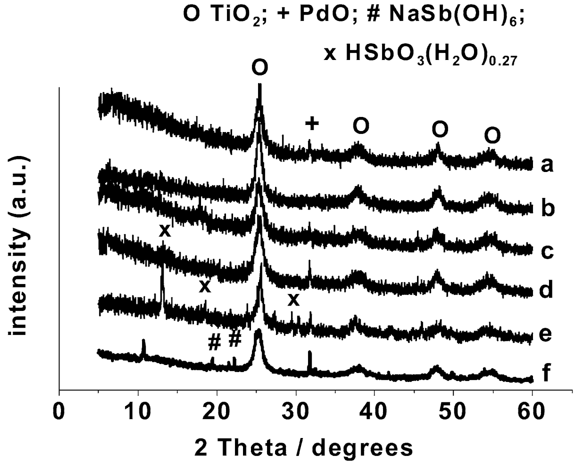


Fig. 1. XRD patterns of fresh Sb–Pd/TiO_2 catalysts (10 wt% Pd loading) with different Sb loadings (a = 4 wt%; b = 6 wt%; c = 8 wt%; d = 12 wt%; e = 16 wt%; f = 20 wt%).

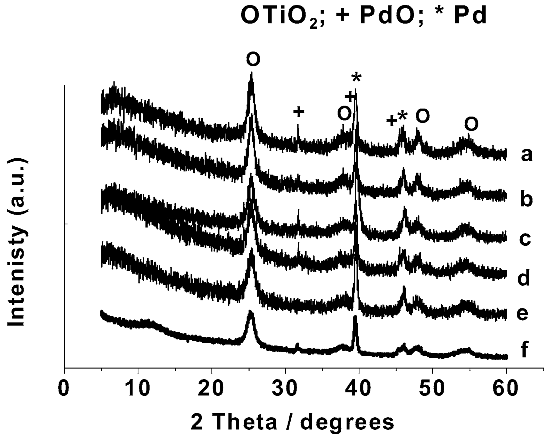


Fig. 2. XRD patterns of used Sb–Pd/TiO_2 catalysts (10 wt% Pd loading, 15–20 h on-stream) with different Sb loadings (a = 4 wt%; b = 6 wt%; c = 8 wt%; d = 12 wt%; e = 16 wt%; f = 20 wt%).

3.2. X-ray diffraction

XRD patterns of the fresh (activated) and used catalysts are depicted in Figs. 1 and 2. In the fresh catalysts, the reflections corresponding to PdO and TiO_2 (anatase) can be seen. In addition, at higher Sb loadings, two more reflections, corresponding to $HSbO_3(H_2O)_{0.27}$ and $NaSb(OH)_6$ phases, are also identified. The formation of such Na-containing Sb phase [$NaSb(OH)_6$] can be expected from the interaction of Na atoms with Sb during activation. Certain amount of Na_2CO_3 was used during preparation to neutralise the acidic catalyst precursor solution.

However, the XRD patterns of used catalysts were somewhat different than those of fresh catalysts. Used catalysts showed reflections belonging to both metallic Pd and PdO. In other words, fresh catalysts contained only PdO phase, whereas the used catalysts contained both Pd and PdO. The appearance of such crystalline metallic Pd species in addition to PdO suggests that the catalysts were undergoing a reduction process on-stream. This observation is well supported by XPS investigations. Furthermore, the other two phases ($HSbO_3(H_2O)_{0.27}$ and $NaSb(OH)_6$), which appeared in the fresh catalysts with high Sb content, have been found to disappear in the used samples. In addition, we found no clues for the formation of any kind of crystalline intermetallic phases between Pd and Sb phases (e.g., Pd_5Sb_2, Pd_3Sb), which are known from the literature [24,31]. The absence of such intermetallic phases in our catalysts might be due to differences in the method of catalyst preparation and conditioning of the solids, such as thermal treatment, pretreatment/activation, and others.

3.3. *Transmission electron microscopy*

Electron micrographs of fresh Sb–Pd/TiO_2 catalysts with different Sb loadings are shown in Fig. 3. The fresh catalyst with 4 wt% Sb loading (Fig. 3a) exhibits only smaller Pd particles with spherical shape and size varying from 1 to 4 nm. However, increased Sb loading to 8 wt% brought about a considerable increase in Pd particle size, which varied in the range of 1–10 nm. Nevertheless, no such proportional increase in the size of Pd particles was observed with further increase in Sb content to 20 wt%. It is worth mentioning that beyond 8 wt% Sb loading, the size of Pd particles decreased considerably, instead of the expected further increase. This observation is also well supported by XPS results obtained on the same samples. The size of most of the Pd particles in these catalysts with high Sb loading (12 and 20 wt%) varied in the range of 1–2.5 nm, compared with 10 nm in the 8 wt% Sb loaded catalyst. Nevertheless, these high-Sb loaded catalysts also contain a few larger (ca. 10 nm), spherical-shaped Pd particles. This result suggests that the presence of Sb has a clear influence on enhancing the size of Pd particles up to an Sb loading of 8 wt%, which, however, seems to be optimum for obtaining materials with the maximum Pd particle size. The morphology of Pd particles is always spherical and remains unchanged irrespective of Sb content, particularly in the fresh samples. On the other hand, the morphology of some of the larger Pd particles is altered in the used catalysts, especially at higher Sb loadings.

To check the influence of Sb presence on Pd particle size, two monometallic catalysts with similar Pd and Sb loadings (i.e., 10 wt% Pd/TiO_2 and 8 wt% Sb/TiO_2) were separately prepared and analysed by TEM; the images are presented in Fig. 4. It is quite interesting to note that the size of Pd particles in the 10 wt% Pd monometallic catalyst was found to be

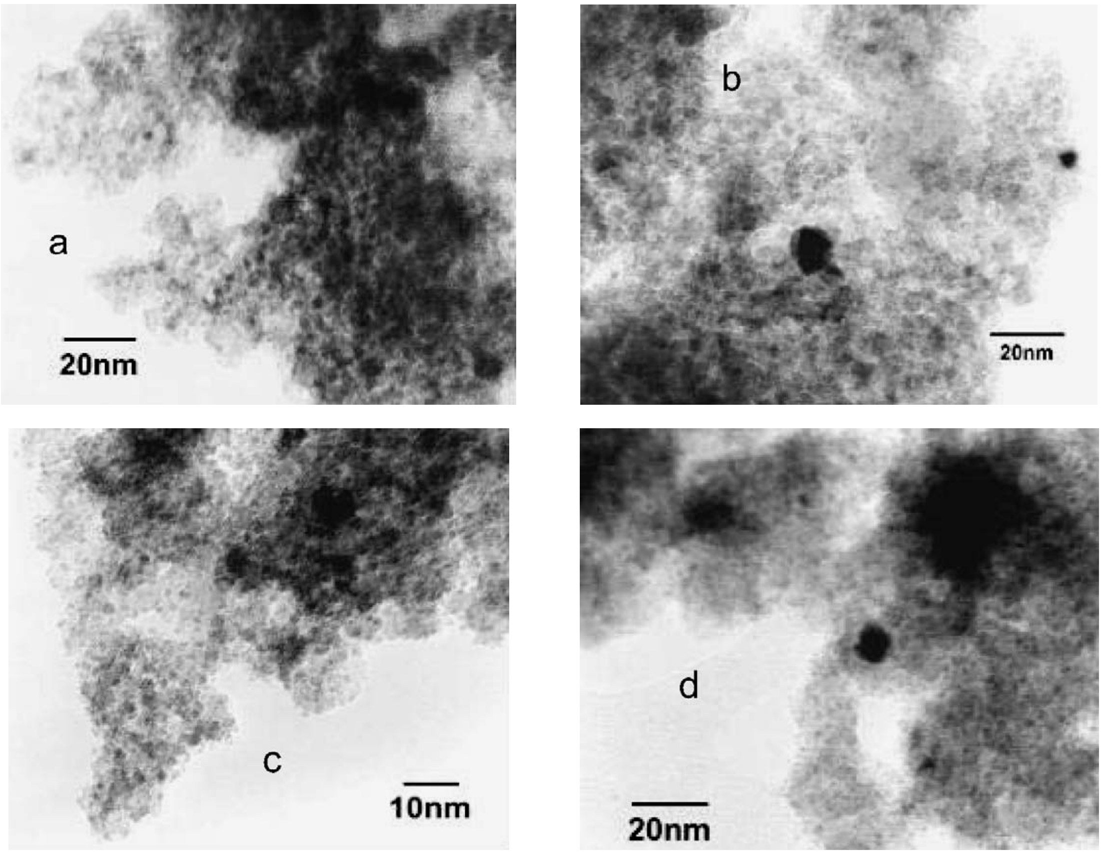


Fig. 3. Electron micrographs of fresh Sb–Pd/TiO_2 catalysts with (10 wt% Pd loading) different Sb loadings (a = 4 wt%, b = 8 wt%, c = 12 wt%, d = 20 wt%).

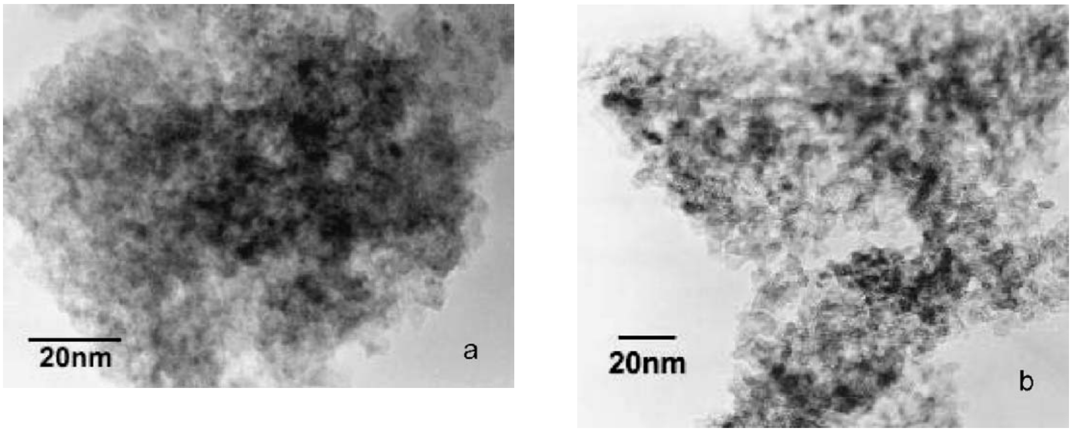


Fig. 4. Electron micrographs of titania supported (fresh) monometallic Sb and Pd catalysts (a = 10% Pd/TiO_2; b = 8% Sb/TiO_2).

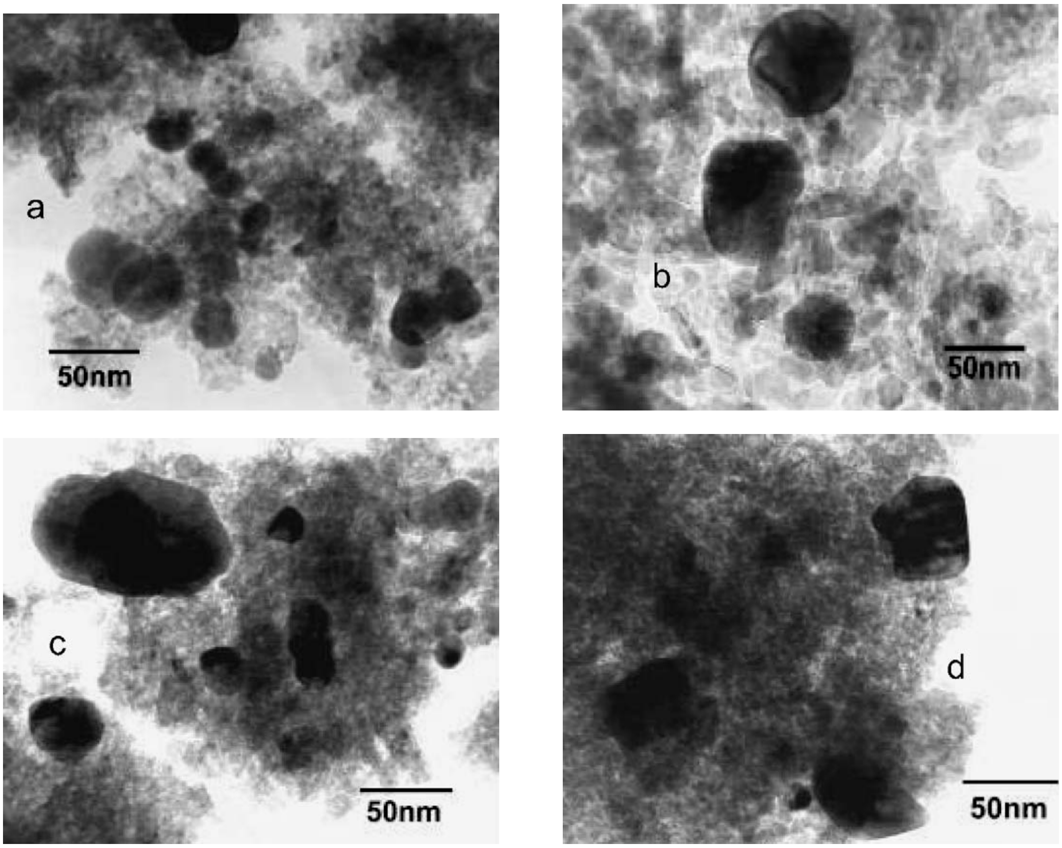


Fig. 5. Electron micrographs of used Sb–Pd/TiO_2 catalysts (10 wt% Pd loading, 15–20 h on-stream) with different Sb loadings (a = 4 wt%, b = 8 wt%, c = 12 wt%, d = 20 wt%).

very small (<1 nm) and even difficult to measure the appropriate size because of weak contrast (Fig. 4a). At the same time, no free Sb particles could be seen in the monometallic Sb sample (Fig. 4b). In the same way, no free Sb particles could be seen in any of the Sb–Pd/TiO_2 catalysts even with higher Sb loadings up to 20 wt%. However, the addition of Sb to Pd resulted in considerably larger Pd particles (1–10 nm). This fact clearly shows that the presence of certain amount of Sb is essential for obtaining a solid with larger Pd particles, which are obviously preferred for better acetoxylation activity, as shown below.

It is quite interesting to note that the size of Pd particles is observed to increase drastically in the used catalysts compared with their corresponding fresh ones. Fig. 5 clearly demonstrates such an effect on the remarkable growth of Pd particles during the course of the reaction due to agglomeration. The used catalyst with 4 wt% Sb showed Pd particles in the range of 15–40 nm, compared to 1–4 nm in the fresh catalyst. It should also be noted that Pd particles up to ca. 90 nm were found in the used catalysts with Sb loading of 8 wt% and above. The shape of Pd particles in both 4 and 8 wt% Sb samples (fresh and used) was found to be almost unchanged and remained more or less spherical (Figs. 5a, 5b). However, the used 12 and 20 wt% Sb catalysts showed some irregular-shaped as well as spherical-shaped Pd particles (Figs. 5c, 5d). The irregular shape of Pd in the used catalysts was observed mainly for the larger particles, whereas the smaller ones remained almost unchanged. It is evident from Figs. 5c, 5d that some of the largest particles tend to form faceting, which is a good sign of reconstruction under the influence of reaction conditions. Similar observations were also reported by Persson et al. [32] in their study on methane combustion over Pd supported on Al_2O_3.

This effect on Pd particle size is possible at two different stages, during the activation of the catalyst (before activity measurements) or during the course of the reaction. To clarify this aspect, the activated catalyst sample as well as the used probe subjected to different stages of reaction (i.e., over a wide range of reaction times) were analysed in earlier studies by TEM [26]. These investigations confirmed that the significant growth in Pd particle size occurred only during the course of the reaction, not during the activation step. Summarising the TEM results, the Sb content of the samples showed an appreciable influence on the size and shape of the Pd particles.

3.4. X-ray photo electron spectroscopy

XPS results of Pd–Sb/TiO_2 catalysts with different Pd loadings at a constant Sb content (8 wt%) were investigated earlier, and interesting observations were found with changing Pd content of the catalysts [26]. Moreover, for higher Pd loadings (i.e., 5, 8, and 10 wt%), a small enrichment of Pd at the near-surface region compared with the bulk was also reported for the fresh catalysts, whereas the agglomeration of Pd particles during the reaction led to a decreased near-surface amount of Pd in the used catalysts [26].

Normalised XP spectra of the Pd 3d state after Shirley background subtraction of the present fresh and used Sb–Pd/TiO_2 catalysts with different Sb loadings are shown in Fig. 6. It is obvious that all of the fresh (activated) catalysts contained exclusively oxidised Pd species (BE = 337.8 eV) at the near-surface region of the catalysts irrespective of Sb loading. This finding is somewhat in line with XRD observations. However, the used catalysts exhibited both metallic (BE = 335.1 eV) and oxidised (BE = 337.6 eV) Pd species in different proportions, indicating a reduction process running during the course of the catalytic reaction. The distribution of these two Pd species in the used catalysts was estimated and is presented in Fig. 7. It is clear from the figure that the near-surface concentration of metallic Pd species decreased from 70 to 50% with increasing Sb loading from 4 to 20 wt%, whereas the oxidised Pd species increased from 30 to 50%; that is, the ratio between these two Pd valence states changed with changing Sb loadings. This result suggests that Sb loading has a considerable influence on catalyst reducibility. Furthermore, the catalysts with high Sb content appeared to stabilise oxidised Pd species to a greater extent than the samples with lower Sb content.

Fig. 8 illustrates the variation of bulk and near-surface Sb/Ti ratios in the fresh and used Sb–Pd/TiO_2 catalysts with different Sb loadings. It is apparent from the figure that both the bulk and near-surface Sb/Ti ratios increased continuously with increasing Sb content of the catalysts, as expected. Interestingly, in the near-surface region (XPS data), the ratios of Sb/Ti, particularly in the fresh catalysts, were increased considerably compared with their corresponding bulk values (ICP-OES data). However, after the catalytic tests, the spent catalysts exhibited considerably lower near-surface Sb/Ti ratios than the corresponding fresh catalysts. This difference was more pronounced in the catalysts with high Sb content (i.e., 12 and 20 wt%). Simultaneously, certain amounts of coke deposits were also observed in the used catalysts. Therefore, such a loss of Sb in the near-surface region can be expected from the covering of catalyst

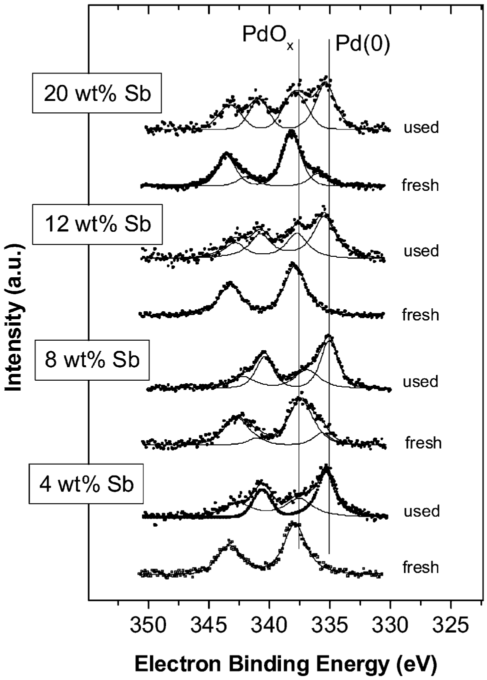


Fig. 6. Normalised XP spectra of the Pd 3d state after Shirley background subtraction of the fresh and used Sb–Pd/TiO_2 catalysts with different Sb loadings.

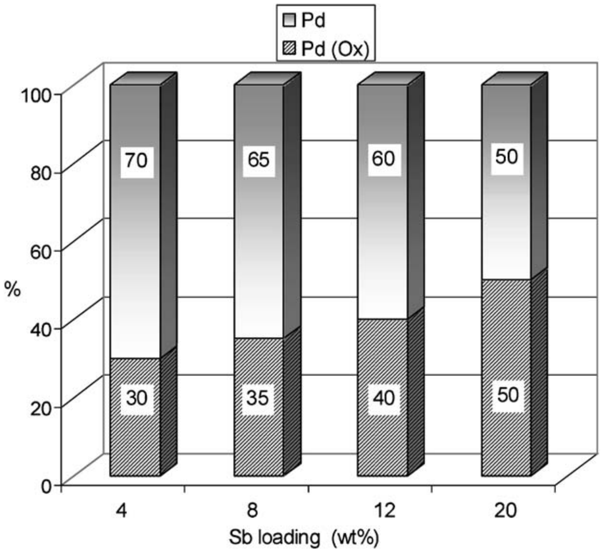


Fig. 7. Near-surface distribution of different Pd species in the used Sb–Pd/TiO_2 catalysts (15–20 h on-stream) with different Sb loadings.

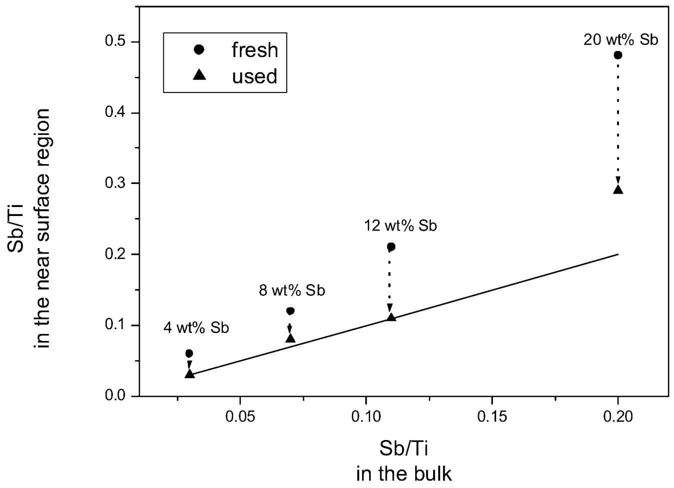


Fig. 8. Variation of bulk to near-surface Sb/Ti ratios in the fresh and used Sb–Pd/TiO_2 catalysts with different Sb loadings.

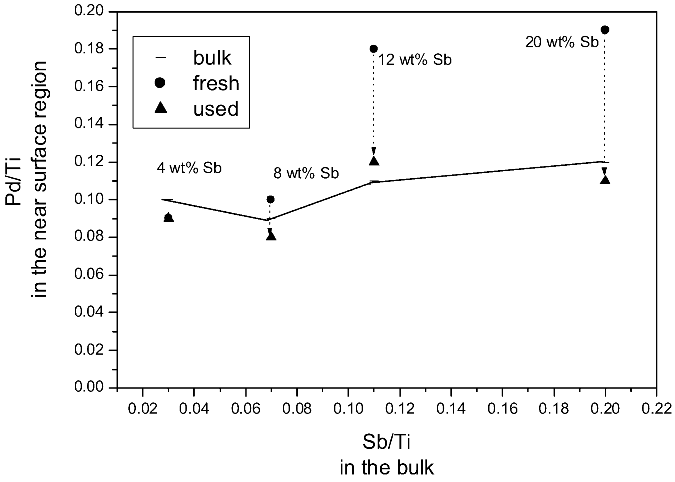


Fig. 9. Pd/Ti ratios as a function of Sb/Ti ratios in the fresh and used Sb–Pd/TiO_2 catalysts with different Sb loadings.

surface by the deposited coke. As also observed in other investigations, Sb remained on the surface in the oxidised form even after the reaction.

Examining the Pd/Ti near-surface values in relation to Sb/Ti bulk values (Fig. 9) shows that Sb loading clearly had a significant influence on the near-surface Pd/Ti ratios obtained by XPS, particularly for fresh catalysts. In addition, the Pd/Ti ratios were more or less constant for the fresh samples up to a Sb loading of 8 wt%, with a sudden jump at loadings above 8 wt%. This result indicates a clear enrichment of Pd in the near-surface region with higher Sb loadings (Fig. 9). TEM analysis of these high-Sb samples gave good supporting evidence for this observation, showing that the Pd particle size decreased beyond 8 wt% Sb loading. Decreased Pd particle size means increased dispersion, which in turn probably leads to increased surface enrichment of Pd. Therefore, such an abrupt jump in near-surface Pd/Ti ratios for the high Sb content catalysts may be attributed to a decrease in Pd particle size.

Interestingly, the near-surface Pd/Ti values estimated in all of the used samples are comparable to their bulk values, but lower than their corresponding fresh samples. This result is again in good agreement with the TEM observations of an increase in Pd particles during the reaction. In addition, no significant differences in the size of Pd particles were observed in the used catalysts with Sb content ranging from 8 to 20 wt%, in which the size of Pd particles remained almost constant at around 90 nm. Therefore, the decrease in near-surface Pd/Ti ratios in the used samples compared with the fresh samples can be attributed to two possible reasons: agglomeration of the Pd particles during the reaction and coke deposition, which leads to covering of active Pd species.

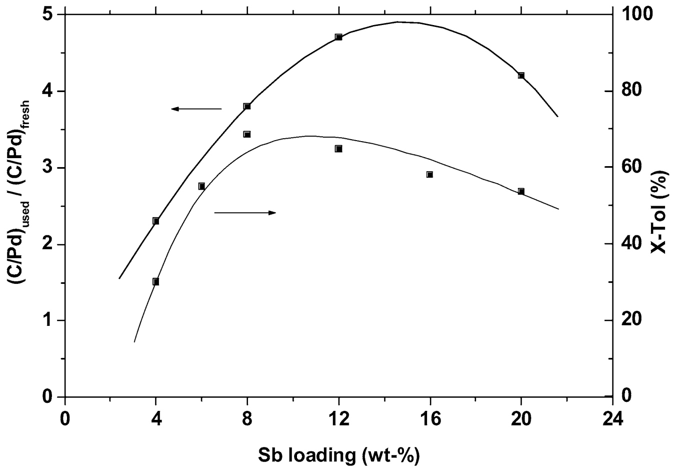


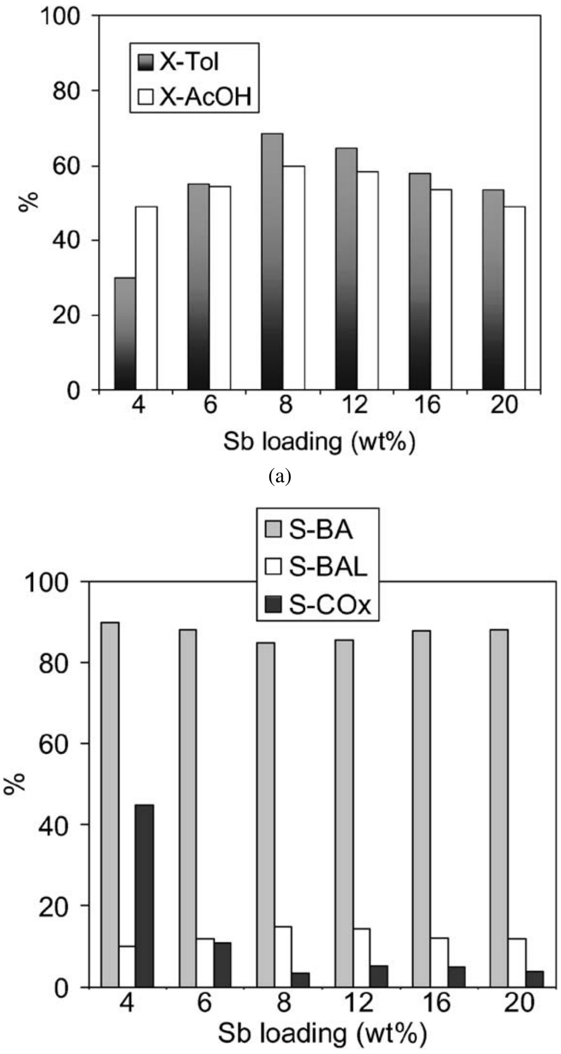
Fig. 10. Variation of the ratio of carbon to palladium (C/Pd) between the fresh and used catalysts as a function of Sb loading in the near-surface region of Sb–Pd/TiO_2 catalysts.

The change in the C/Pd ratio in the used and fresh catalysts (carbon proportions are always measured on fresh samples, because of contamination of sample surface by, for example, organic compounds or carbon dioxide during storage on air) as a function of Sb loading is depicted in Fig. 10. The conversion of toluene obtained from the acetoxylation runs is also correlated with Sb loading in this figure. It is evident that the deposition of coke on Pd surface depends on the amount of Sb present in the catalysts. The ratio of C/Pd increased from 2.3 to 4.7 with an increase in Sb content from 4 to 12 wt%. A slight decrease to 4.2 was observed with a further increase in Sb loading to 20 wt%. These results of coke deposition (Fig. 10) are also reflected in the catalyst activity. The conversion of toluene increased continuously with Sb loading up to 8 wt% and then decreased slightly. However, an exact correlation as that of the tendency of C/Pd ratios was not seen. Summarising these findings, the valence states of Pd and the coke deposition were influenced considerably by the Sb concentration in these catalysts.

3.5. Catalytic activity

3.5.1. Influence of Sb loading on the toluene acetoxylation activity of Sb–Pd/TiO_2 catalysts

Figs. 11a and 11b compare the conversion levels of reactants and selectivities of products as functions of Sb loading. The conversion of toluene increased from 30 to 68% with in-



(a)

(b)

Fig. 11. (a) Influence of Sb loading on the catalytic performance of Sb–Pd/TiO_2 catalysts ($T = 210\,^{\circ}C$; GHSV (STP) = 2688 h^{-1}; $\tau = 1.34$ s; mole ratio of Tol:AcOH:O_2:inert gases (N_2 + Ar) = 1:4:3:16; X-Tol = conversion of toluene, X-AcOH = conversion of acetic acid). (b) Influence of Sb loading on the catalytic performance of Sb–Pd/TiO_2 catalysts ($T = 210\,^{\circ}C$; GHSV (STP) = 2688 h^{-1}; $\tau = 1.34$ s; mole ratio of Tol:AcOH:O_2:inert gases (N_2 + Ar) = 1:4:3:16; S-BA = selectivity of benzyl acetate, S-BAL = selectivity of benzaldehyde; S-CO_x = selectivity of carbon oxides).

creased Sb loading from 4 to 8 wt% due to an increase in Pd particle size of fresh catalysts, and then decreased to 54% with a further increase in Sb loading to 20 wt%. In a similar way, the conversion of acetic acid also increased from 49 to 60% with an increase in Sb loading to 8 wt% and then decreased again to 49% with a further increase in Sb content to 20 wt% (Fig. 11a). The selectivity of BA was independent of conversion of toluene and remained more or less constant (85–90%) regardless of Sb loading of the catalysts indicating highly selective nature of the reaction. Therefore, the yield of BA changed in a similar fashion as that of conversion of toluene. The maximum yield of BA obtained over 8 wt% Sb catalyst was close to 60%. Benzaldehyde was the main byproduct of the reaction, and its selectivity varied in the range of 10–15%. It is noteworthy that the selectivity of total oxidation products (CO_x) was decreased significantly, from ca. 45% to <5%, with an increase in Sb loading up to 8 wt% and then remained more or less constant at this level with further increase in Sb loading to 20 wt% (Fig. 11b). Nevertheless, one should take into account that the formation of such high amount of CO_x observed for low Sb loaded sample was due mainly to oxidative decomposition of acetic acid rather than toluene, as indicated by the high conversion of acetic acid (ca. 49%) compared with toluene (30%) over the same catalyst (4 wt% Sb). Separate experiments also proved that the formation of CO_x occurred mainly from the oxidative decomposition of acetic acid, and not from toluene. The finding that the decomposition of acetic acid was the main reason for the formation of CO_x, whereas the contribution of toluene toward CO_x formation was negligible under these reaction conditions, has also been reported previously [26].

The increase in catalytic activity up to 8 wt% Sb may be attributed mainly to an increase in Pd particle size, whereas the decrease in activity with further increase in Sb content might be due to various factors, including the presence of high Sb near-surface concentrations (Sb/Ti ratios), a change in the valence state (redox properties) of Pd, a change in the morphology of larger Pd particles, dilution of active Pd species (i.e., formation of smaller particles), and weakened interactions. From this study, 8 wt% Sb appears to be the optimum for obtaining the best catalyst activity. Nevertheless, these catalysts deactivated with time on stream due to coke deposits, which in turn caused loss of both Pd and Sb in the near-surface region. The amount of coke decreased marginally from 5 to ca. 3% with an increase in Sb loading from 4 to 20 wt%. In other words, less coke was observed for higher Sb content catalysts at almost similar durations of catalytic testing (15–20 h).

Note that the presence of Sb in appropriate amounts led to an increase in activity, whereas excess Sb exerted a detrimental effect. Various researchers also found such correlations between activity and the amount of the co-component on similar and different systems for different acetoxylation reactions. A study by Shinohara [10] on the influence of Sb/Pd ratio for the gas-phase acetoxylation of 1,3-butadiene over Pd–Sb–KOAc catalysts found that the activity increased up to a Sb/Pd ratio of 0.4 and then decreased rapidly with further increase (ca. 2.5). Shinohara claimed that Pd and Sb were interacting with each other and such interaction led to the improvement in both activity and selectivity. He also reported that excess Sb loading caused a decrease in activity by covering the active species. Benazzi et al. [13] investigated the influence of Sn/Pd ratio in catalysts for liquid-phase acetoxylation of toluene and reported that the activity was continuously increased from ca. 10 to >90% with an increase in Sn/Pd ratio from 1 to 5 and then decreased with a further increase in Sn/Pd ratio. Tanielyan et al. [21] found in their investigations on liquid-phase acetoxylation of toluene that the catalyst behaviour was unstable at lower Sn/Pd ratios (<2), noting dissolution of Pd into the liquid phase. These authors also reported that a higher Sn/Pd ratio (>2) improved the stability of the surface complexes and that the excess Sn also decreased the coordinative unsaturation of the Pd atoms and thus decreased their catalytic activity. In another study, these same authors also proposed that Sn not only was involved in the reduction of palladium, but also influenced the size and morphology of metallic palladium [33]. In a similar way, the present study also showed an appreciable influence of Sb on Pd particle size, morphology, and catalytic performance.

In accordance with our earlier observations [25,26,28], the active Pd site needed to be of a certain critical size to catalyse the acetoxylation reaction. Too-small particles (of a few nm) do not have faces of this required size and hence are not active for the desired reaction. Sb as a co-component positively influenced the size of Pd particles. In addition, XPS showed (Fig. 7) that Sb stabilised the oxidised state of Pd during the reaction, perhaps due to synergistic effects between Pd and Sb. The exact reasons for the formation of relatively smaller Pd particles for high Sb loadings (e.g., 20 wt%) observed for the fresh samples remain unclear. Further investigations are needed to uncover this effect and to gain better insight into the precise interaction between Sb and Pd.

Some interesting observations can be made by comparing the influence of Pd loading (0.5–20 wt% Pd) from the earlier study [26] and the Sb loading from the present study (4–20 wt%) in terms of activity enhancement versus Pd particle size. In earlier investigations, it was observed that both catalytic activity and Pd particle size increased continuously up to 20 wt% Pd. In contrast, in the present study, the activity and the size of Pd particles increased only up to 8 wt% Sb and then decreased with further increase in Sb loading. One common feature of these two systems is that the catalytic activity changes in concert with the changes in Pd particle size. Therefore, it can be concluded that the size of Pd particles has a clear influence on the catalytic performance, and that larger particles provide better performance. Another common feature of these two systems is that the selectivity of BA is independent of the conversion of toluene. From these results, it can be inferred that larger Pd particles are necessary only for better activity.

3.5.2. Comparison of catalytic performance of fresh and regenerated Sb–Pd/TiO$_2$ catalysts with different Sb loadings

It is obvious from Table 2 that the materials regenerated by removing coke deposits under air atmosphere restored their maximum activity, which had been lost due to coking. It is quite amazing that the conversion of toluene and the yield of BA observed for the fresh and regenerated catalysts are very comparable. Therefore, it can be deduced that the regeneration process (250 °C/2 h/air) is very effective. It has been shown [26] that the regeneration process has no affect on the size of Pd particles, and hence no considerable difference in the size of Pd particles was observed between the regenerated and deactivated catalysts.

3.5.3. Comparison of time-on-stream behaviour of Sb–Pd/TiO$_2$ catalysts with different Sb loadings

Comparisons of conversion of toluene and the selectivity of BA with time on stream over the low-loaded (4 wt% Sb), high-loaded (20 wt% Sb), and optimum-loaded (8 wt% Sb) catalysts are presented in Fig. 12. It is quite interesting to note that the catalysts irrespective of Sb loading showed a similar tendency toward changing activity and selectivity behaviour with time on stream. It is evident from the figure that all of the catalysts had very low initial activities, which increased with time, undeniably due to an increase in Pd particle size, as evidenced by TEM analysis. Nevertheless, as shown above, the selectivity of BA was independent of the conversion of toluene and varied between 85 and ca. 90%. The only difference in performance of these three catalysts was in the conversion levels, which depended on the size of Pd particles, which was again dependent on Sb loading, as mentioned earlier. The order of decrease in the size of Pd particles in the fresh catalysts was as follows: 8 wt% Sb > 20 wt% Sb > 4 wt% Sb; that is, the catalyst with the smallest Pd particles (4 wt% Sb) exhibited the lowest conversion of toluene (X-Tol = ca. 30%), and the catalyst with the largest Pd particles had the highest conversion of toluene (X-Tol = 68%). Yet another interesting observation is that the time needed for the growth of Pd particles to their maximum size (90–100 nm) also depended on the Sb content in these samples. As can be clearly seen from Fig. 12, the catalyst exhibiting low activity with low Sb content (4 wt% Sb) contained small Pd particles and took less time to attain steady-state conditions and displayed maximum activity compared with the catalysts showing higher activity with larger Pd particles. For instance, the

Table 2

Comparison of performance of fresh and regenerated Sb–Pd/TiO$_2$ (anatase) catalysts with different Sb loadings in toluene acetoxylation (toluene conversion (X-Tol/%), benzyl acetate yield (Y-BA/%), benzyl acetate selectivity (S-BA/%))

Sb (wt%)	Fresh catalysts			Regenerated catalysts		
	X-Tol/%	Y-BA/%	S-BA/%	X-Tol/%	Y-BA/%	S-BA/%
4	30.0	27.0	90.0	28.8	26.2	91.0
6	55.0	48.4	88.0	53.4	47.9	87.6
8	68.5	58.0	85.0	68.0	58.0	85.0
12	64.7	55.4	85.6	64.9	56.1	86.5
16	58.0	50.9	87.7	57.7	49.9	86.5
20	53.6	47.2	88.0	53.8	47.1	87.6

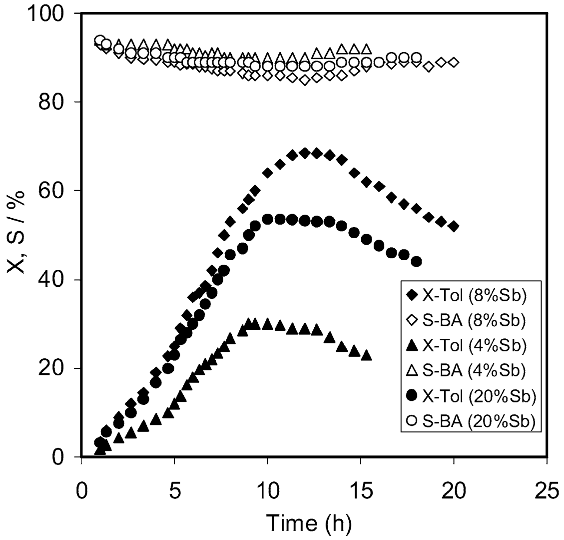


Fig. 12. Comparison of time-on-stream analysis of Sb–Pd/TiO$_2$ catalysts with various Sb loadings ($T = 210\,^{\circ}\mathrm{C}$; GHSV (STP) = 2688 h^{-1}; $\tau = 1.34$ s; mole ratio of Tol:AcOH:O$_2$:inert gases (N$_2$ + Ar) = 1:4:3:16; X-Tol = conversion of toluene, S-BA = selectivity of benzyl acetate).

Table 3
Pd particle size, near-surface Sb/Ti and Pd/Ti ratios in the fresh and used Sb–Pd/TiO_2 catalysts with different Sb loadings

Sb (wt%)	Pd size (nm)		Sb/Ti (surface)		Pd/Ti (surface)	
	Fresh	Used	Fresh	Used	Fresh	Used
4	1–4	15–40	0.06	0.03	0.09	0.09
8	1–10	90–100	0.12	0.08	0.10	0.08
20	2.5 (10*)	90–100	0.48	0.29	0.19	0.11

* A few bigger particles of 10 nm.

4 wt% Sb catalyst displayed maximum activity with in <10 h, whereas the other two catalysts took relatively longer (i.e., ca. 10 h for 20 wt% Sb and >10 h for 8 wt% Sb) to exhibit maximum activity according the associated Pd particle size. Such deviations in time required to attain steady-state conditions indicate that the content of Sb influenced not only the size of Pd particles, but also the valence states of Pd and hence the redox properties of Pd (see Fig. 7). As pointed out earlier, the low reducible nature of oxidised Pd species, particularly at higher Sb content, seems to be another possible reason for the longer time to display maximum activity. This difference in the time needed to grow to maximum size and attain steady-state conditions might also depend on the change in surface valence states of Pd, which is discussed below in more detail. However, the change in Pd particle size was a dominant factor in altering catalyst performance, in good agreement with earlier findings obtained over different catalyst systems.

Although there was no significant difference in Pd particle size between the spent 8, 12, and 20 wt% Sb catalyst, these catalysts displayed some differences in catalytic performance. If Pd particle size alone was responsible for better performance, then all of the catalysts with high Sb loadings (8 wt% and above) should exhibit similar maximum conversion of toluene. However, the 8 wt% Sb catalyst displayed maximum activity compared with the 12 and 20 wt% Sb solids. This result suggests that in addition to Pd particle size, there should be other parameters would also be expected to have a considerable influence on catalyst performance. The results in Table 3 give additional information indicating that the presence of higher Sb concentrations (i.e., Sb/Ti) at the near-surface region had an unfavourable effect on the catalytic performance of particularly high Sb solids. It is also apparent from Table 3 that the Sb/Ti ratio increased with an increase in Sb loading, whereas the Pd/Ti ratio remained more or less constant (ca. 0.1 in all samples) due to the constant proportion of Pd (10 wt%) in all these catalysts. Therefore, the decline in catalytic activity with an increase in Sb loading beyond 8 wt% can be attributed to increased surface Sb concentration compared with Pd.

4. Conclusions

The results of these investigations demonstrate a clear description of Sb loading-dependent activity and confirm that Sb loading is a key parameter in governing the catalytic properties of Sb–Pd/TiO_2 solids used as catalysts for the acetoxylation of toluene to benzyl acetate. The results also demonstrate a distinct influence of Sb loading on the size of Pd particles, valence states of Pd (reducibility), surface C/Pd ratios, and morphology (faceting). Of all of these effects, Pd particle size has a somewhat dominant influence on catalytic performance. Our investigations clearly show that the low initial activities of the catalysts are due simply to the presence of smaller Pd particles, whereas a gradual increase in activity with time on stream can be attributed to an increase in Pd particle size. However, the decrease in activity within only a few hours of attaining steady-state conditions can be ascribed to coke deposits. Moreover, the deactivated (used) catalysts can be easily regenerated in air to restore their high catalytic activity. Interestingly, the used catalysts had significantly larger Pd particles (90–100 nm) than the corresponding fresh catalysts (1–10 nm) due to agglomeration and restructuring of Pd during the course of the reaction. Either the absence of Sb or its presence in lower amounts directs the reaction in an unselective way, resulting in the formation of CO_x as a major product of the reaction; that is, total oxidation becomes a predominant reaction. Nevertheless, such deep oxidation caused by oxidative decomposition of acetic acid can be effectively suppressed by optimising Sb loading. Therefore, identifying the optimum Sb loading is essential to enhance the catalytic activity of the solids. The current study found that 8 wt% Sb was optimum in view of its better performance. A further increase in Sb loading up to 20 wt% led to slightly decreased conversion but with more or less unchanged product selectivities. Further studies are in preparation using in situ methods, such as XAS and XRD, under catalyst working conditions to gain deeper insight into the precise nature of interaction between Sb and Pd and its influence on the dynamic behaviour of Pd species (e.g., changes in particle size, valence states [reducibility], morphology [faceting]) in controlling and fine tuning the catalytic properties of the catalysts.

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