Catalysis Today 141 (2009) 317–324

Contents lists available at ScienceDirect

Catalysis Today

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

Palladium-catalysed vapour phase aerobic acetoxylation of toluene to benzyl acetate

V. Narayana Kalevaru [*], A. Benhmid, J. Radnik, M.-M. Pohl, B. Lücke, A. Martin

Leibniz-Institute for Catalysis (former ACA), Richard-Willstätter-Str. 12, D-12489 Berlin, Germany

ARTICLE INFO

Article history:
Available online 14 July 2008

Keywords:
Gas phase acetoxylation
Pd-containing catalysts
Varying Pd and Sb contents
Effect of support
Deactivation
Pd particle size effects

ABSTRACT

Supported Pd–Sb acetoxylation catalysts with different Pd and Sb amounts as well as varying supports were prepared by impregnation technique. The contents of Pd and Sb are varied over a wide range, for instance Pd is varied from 0.5 to 20 wt% by keeping Sb content at 8 wt%. In a similar way, Sb content is varied from 4 to 20 wt% by keeping Pd loading constant at 10 wt%. Four different supports such as TiO_2, γ-Al_2O_3, SiO_2 and ZrO_2 are applied at constant Pd (10 wt%) and Sb (8 wt%) contents. Catalytic performance of these solids is evaluated for the gas phase acetoxylation of toluene to benzyl acetate (BA) at $T = 210\ ^\circ C$ and $p = 2$ bar. XPS revealed a considerable loss of both Pd and Sb in the near-surface region in the used catalysts. TEM showed that Pd particles exhibit spherical morphology and their size increased dramatically in the spent catalysts compared to their corresponding fresh ones. Monometallic catalysts showed very poor acetoxylation performance but high total oxidation, which results in an increase of the yield of CO_x up to ca. 50%. However, combination of both Pd and Sb was found to suppress total oxidation and thereby enhance the acetoxylation performance with high BA selectivity of $\geq 85\%$. Catalytic activity was observed to increase continuously with increase in Pd loading. The catalyst with the highest Pd loading (20 wt% Pd) displayed the best performance (toluene conversion = > 90%, BA yield = > 75%). The activity is however decreasing with time-on-stream due to coke deposits. Nevertheless, the deactivated samples can be regenerated in air to restore their maximum activity. Nature of support, content of co-components showed strong influence on the catalytic performance.

1. Introduction

In general, acetoxylation refers to a process wherein an alkyl group is converted into an ester group in a single step in presence of air (or oxygen containing feed) and acetic acid under suitable reaction conditions. A representative example of such process is the acetoxylation of toluene to benzyl acetate (BA) over Pd-containing catalysts. However, depending upon the reaction conditions and the type of catalyst applied, the oxidation of toluene can be diverted in three different ways [1,2] such as (i) arylic coupling to give bitolyl, (ii) ring acetoxylation to tolyl acetate and (iii) side chain acetoxylation to benzyl acetate. Our interest lies in the third direction with a special emphasis devoted to produce selectively benzyl acetate from toluene in a single step (Scheme 1). The vapour phase acetoxylation of toluene in particular is an interesting research field from both academic and industrial viewpoints. The target product, BA, is widely used in perfumery, food and chemical industries. In the present reaction, BA is the target product and the other possible by-products that are expected from this reaction are benzaldehyde (BAL), CO_x and H_2O. Though benzaldehyde is a by-product, it is also a product of industrial importance. In addition, this route shown in Scheme 1 also provides the possibility of further producing benzyl alcohol by the hydrolysis of BA.

Acetoxylation of simple olefins like ethylene to vinyl acetate (e.g. [3]) and propylene to allyl acetate [4] are known from the literature. However, the extension of this work from simple olefins to aromatics (with a particular reference to toluene to benzyl acetate) is still under developmental stage. Conventionally, BA is produced by chlorine route, which involves multi-steps such as (i) the chlorination of toluene to chlorotoluene, (ii) hydrolysis of chlorotoluene by NaOH to benzyl alcohol and (iii) esterification of benzyl alcohol with acetic acid to give BA. Furthermore, this route also produces certain amounts of harmful by-products (e.g. HCl)

---

[*] Corresponding author. Tel.: +49 30 6392 4315; fax: +49 30 6392 4454.
E-mail address: narayana.kalevaru@catalysis.de (V.N. Kalevaru).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.06.004

Scheme 1.

and thus becomes environmental unfriendly process. On the other hand, the current gas phase acetoxylation of toluene is more green and clean process.

Literature survey reveals that Pd-based catalysts are normally used for acetoxylation reactions [5–9]. Moreover, addition of second metallic component, amount of metal content, particle size of Pd, nature of support, etc. are some of the key parameters that can greatly influence the catalytic performance of the catalysts. From previous investigations [10], it has been observed that the combination of Sb to Pd displayed improved activity and selectivity. The primary aim of this study is to develop highly active and selective catalysts and try to overcome the major problem of catalyst deactivation. In this contribution, we address the various issues related to catalytic performance such as influence of metal contents (Pd and Sb), nature of support used, deactivation problems, Pd particle size effects and so on.

2. Experimental

2.1. Catalyst preparation

A variety of supported Pd–Sb catalysts are prepared by impregnation in two steps. Required amount of $SbCl_3$ is impregnated in the first step on to the TiO_2 (anatase) support (BET surface area = 315 m^2/g) followed by $PdCl_2$ in the second step. The metal contents of Sb and Pd are varied in the range from 4 to 20 wt% Sb (at 10 wt% constant Pd) and 0.5 to 20 wt% Pd (at 8 wt% constant Sb) of the total catalyst, respectively. Investigations on varying contents of Pd and Sb are made only with TiO_2 (anatase) support. Additionally, three different supports such as γ-Al_2O_3 (BET surface area = 249 m^2/g), SiO_2 (BET surface area = 392 m^2/g) and ZrO_2 (BET surface area = 206 m^2/g) were also used at fixed loadings of Pd and Sb (10 and 8 wt%) and compared their performance with that of TiO_2-supported catalyst with similar Pd and Sb loadings. All the supports used were commercial samples. More information on the catalyst preparation and other details of the applied materials are reported elsewhere [11].

2.2. Catalytic tests

Catalytic tests were carried out in a fixed bed tubular stainless steel reactor at $T = 210\,^\circ C$ and $p = 2$ bar. About 1 ml of catalyst particles (0.425–0.6 mm fraction) is loaded into the reactor and activated in airflow (27 ml/min) at 300 °C for 2 h prior to activity measurements. The reactant feed mixture consists of argon, synthetic air, toluene and acetic acid. The flow rates of gaseous reactants (Ar, air) are measured using mass flow controllers, while the liquid reactants such as toluene and acetic acid were dosed using HPLC pumps. The following molar ratios of the reactants are applied, i.e. toluene:acetic acid:oxygen:inert gas = 1:4:3:16. The product stream was collected for every half an hour and analysed on-line by GC using FID [12]. Total oxidation products (CO_x) were estimated using methaniser.

3. Results and discussion

3.1. Catalyst characterisation

BET surface areas of Pd–8Sb/TiO_2 catalysts are observed to decrease from 161 to 42 m^2/g with increase in Pd loading from 0.5 to 20 wt%. Similar such tendency is also observed with varying Sb contents of Sb–10Pd/TiO_2 solids. XRD has shown the presence of both Pd and PdO phases in these samples particularly with high Pd loadings (ca. 10 wt% and above). TEM showed that fresh catalysts contain smaller Pd particles in the range from 1 to 20 nm, which however depends on the metal content of the catalysts. The particle size of the fresh catalysts reveals a narrow size distribution, and the morphology of Pd-containing particles is spherical. Used catalysts exhibited significantly bigger Pd particles up to 100 nm compared to their corresponding fresh samples due to agglomeration of Pd during the course of the reaction. XPS indicated that the catalytic reaction leads to a shift in the Pd 3d spectra of the used samples to lower binding energies signifying changes in the valence states of Pd species.

3.2. Synergistic effects between Pd and Sb in Pd–Sb/TiO_2 catalyst

During the initial stages of the work, we have carried out a set of preliminary experiments using monometallics such as Pd/TiO_2 and Sb/TiO_2, as well as pure TiO_2 under identical reaction conditions. Fig. 1 illustrates that monometallic Pd and Sb catalysts are found to be almost inactive, giving remarkably poor acetoxylation performance. Pure TiO_2 is nearly inactive as expected and at the same time 8% Sb/TiO_2 also gave very poor performance (X-Tol = $<$ 2%). Similarly, 5% Pd/TiO_2 also displayed only 2% conversion of toluene but remarkably high CO_x. In other words, this catalyst displayed very low conversion of toluene, while high yield of CO_x ($>$50%) and high conversion of acetic acid (X-AcOH = 53.9%). This fact suggests that the formation of CO_x is mainly occurring from the oxidative

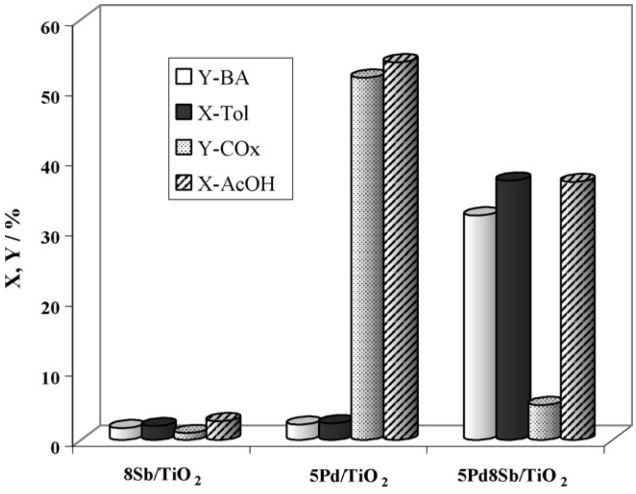

Fig. 1. Synergistic effects between Pd and Sb in Pd–Sb/TiO_2 catalysts.

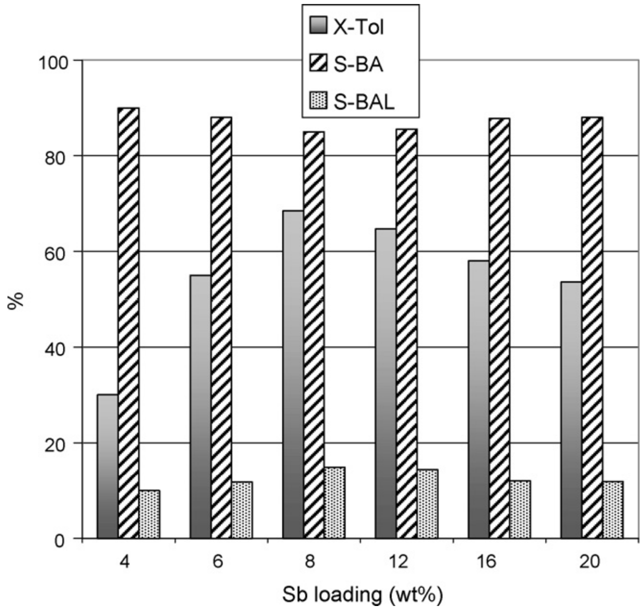

Fig. 2. Influence of Sb loading on the catalytic performance of Sb–10Pd/TiO_2 catalysts with different Sb loadings.

decomposition of AcOH, but not from toluene. Separate experiments also confirmed this assumption. On the other hand, combination of both Pd and Sb showed an amazing effect on performance and completely changed the direction of the reaction in a more selective way, i.e. the yield of CO_x is drastically reduced (by a factor of 10) from over 50% to just 5%, while the yield of BA remarkably increased (by a factor of 16) from about 2% to over 30%. In addition, X-AcOH also reduced from 54 to ~35%. Such promotional effect was assigned to synergistic effects between Pd and Sb, which is probably due to modification of redox properties.

After obtaining such an amazing performance of Pd–Sb composition, in the next step two different series of catalysts were prepared by varying both Pd and Sb contents over a wide range. In the first series, Sb is varied from 4 to 20 wt% while the content of Pd is kept constant at 10 wt%. In the second series, Sb content is kept constant at 8 wt% and Pd is varied from 0.5 to 20 wt% of the total catalyst.

3.3. Influence of Sb loading on the acetoxylation activity of Sb–10Pd/TiO_2 catalysts

It is evident from Fig. 2 that the Sb loading has a distinct influence on the catalytic performance. The conversion of toluene was found to increase from 30 to 68% with increase in Sb loading from 4 to 8 wt% and then decreased to 54% with further increase in Sb loading to 20 wt%. In a similar way, the conversion of acetic acid (not shown here) is also enhanced first from 49 to 60% up to 8 wt% Sb loading and then decreased again to 49% with further increase in Sb content to 20 wt%. However, the selectivity of BA is found to be independent on conversion of toluene and remains more or less constant (85–90%) regardless of Sb loading. Therefore, the yield of BA is observed to change exactly in a similar fashion as that of conversion of toluene. The maximum yield of BA obtained over 8 wt% Sb catalyst is close to 60%. Benzaldehyde is the main by-product and its selectivity is varied in the range from 10 to 15%. Interestingly, the Pd particle size of fresh catalysts is also changed in a similar way as that of catalytic activity. Nevertheless, these catalysts are found to deactivate with time-on-stream due to coke deposits, which in turn cause a loss of both Pd and Sb in the near-surface region. Though it is not shown here, it is worthwhile to comment that the selectivity of total oxidation products (CO_x) was remarkably decreased from ca. 45 to <5% with increase in Sb loading up to 8 wt% and then remains more or less constant at this level with further increase in Sb loading to 20 wt%. Nevertheless, one should take into account that the formation of such high amount of CO_x observed for low Sb loaded sample is mainly due to oxidative decomposition of acetic acid rather than toluene, which is also evidenced from high conversion of acetic acid (ca. 49%) compared to toluene (30%) over low Sb-containing catalyst (4 wt% Sb).

The increase in catalytic activity up to 8 wt% Sb may be attributed mainly to an increase in Pd particle size, while the decrease in the activity with further increase in Sb content might be due to various reasons such as the presence of high Sb concentration in the near-surface regions (Sb/Ti ratios higher than Pd/Ti), change in the valence state (redox properties) of Pd, change in the morphology of bigger Pd particles, dilution of active Pd species at higher Sb loadings etc. Analysis of coke in the spent samples indicates that relatively less amount of coke (i.e. 5% coke in 8 wt% Sb and ~3% in 20% Sb) is observed for higher Sb content catalysts for almost similar duration of catalytic tests (15–20 h). It is noticed that the presence of Sb in appropriate amounts is a crucial, while an excess amount of Sb has a detrimental effect. From this study, it appears that 8 wt% Sb is optimum for obtaining the better activity of the catalysts. Similar such observations are also made by other researchers on optimising the amount of co-components on the acetoxylation performance of similar such and different catalytic systems and acetoxylation reactions [2,13]. XRD analysis showed the formation of $HSbO_3(H_2O)_{0.27}$ phase in the fresh SbPd/TiO_2 samples having high Sb contents (≥12 wt% Sb). However, this phase is found to disappear in the spent samples and then no other additional Sb-containing phases were found. It should also be noted that neither Pd–Sb alloys/intermetallics nor crystalline Sb-oxides/mixed oxides with Pd are found in these samples. These phases are generally reported from literature. Formation of such phases however depends on the thermal treatments such as calcination temperature, duration of calcination and atmosphere. The mild calcination conditions (300 °C/2 h/air) applied in the present study seems to be the main reason for the absence of those expected Sb-containing crystalline phases. However, XPS revealed that the Sb is present always in its oxidised state with the binding energy value of 540.1 eV in the fresh sample and 539.9 eV in the spent sample (after 22 h-on-stream), which indicates that the Sb is in oxidised state (between +3 and +5). In other words, no considerable changes occurred in the valance state of Sb between fresh and used samples.

3.4. Influence of Pd loading on the acetoxylation activity of Pd–8Sb/TiO_2 catalysts

After restricting our initial choice to Pd–Sb/TiO_2 system, we further explored the influence of Pd loading on the catalytic performance over a wide range of Pd contents (0.5–20 wt%). The results presented in Fig. 3a show that the Pd loading has a promotional effect on the conversion of toluene, which has increased remarkably from 16 to ca. 93% with increase in Pd content from 0.5 to 20 wt%. The selectivity of desired product, BA, is observed to remain more or less constant at around 85% and is independent of toluene conversion. Thus, the yield of BA is also observed to change in a similar fashion as that of conversion of toluene and reached a value close to 80%. This tendency is in good agreement with those observed above for Sb–Pd catalysts with varying Sb contents (Fig. 2). As mentioned earlier, BAL is the major

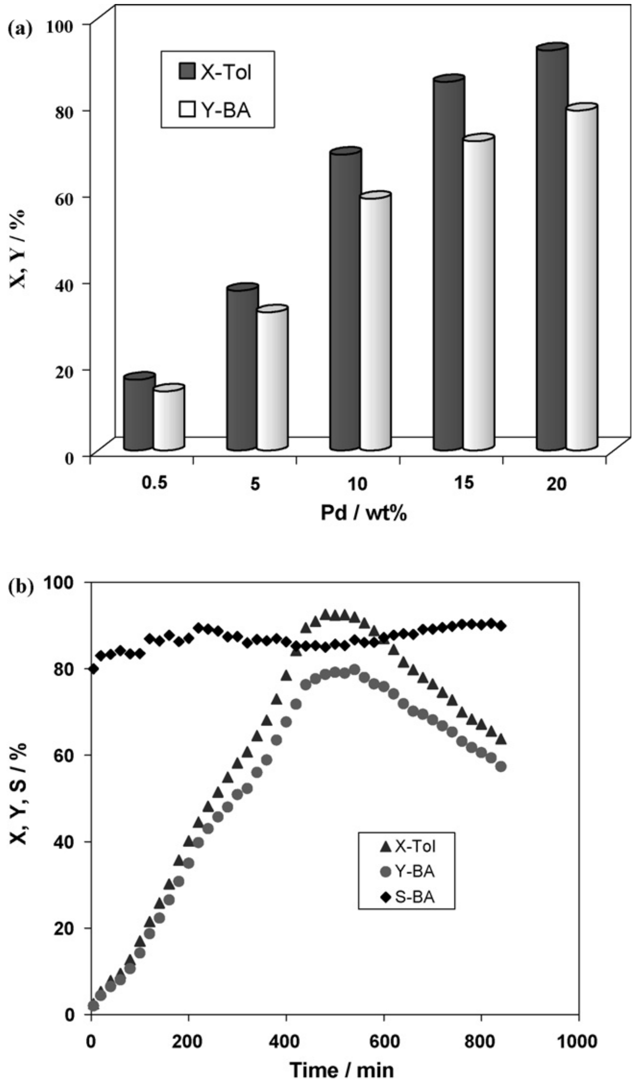

Fig. 3. (a) Influence of Pd loading on the catalytic performance of Pd–8Sb/TiO_2 catalysts; (b) variation of catalytic performance of 20Pd–8Sb/TiO_2 catalyst with time-on-stream.

by-product and the remaining products are total oxidation products. S-BAL is varied in the range from 10 to ∼15%. The larger Pd particles are always found to be critical for better performance. Though we were able to achieve significantly high conversion of toluene and yield of BA, all these catalysts still suffer from a major problem of catalyst deactivation after several hours of operation. Our analysis of deactivated catalysts disclosed that the catalyst deactivation is mainly due to coke deposition on the catalyst surface. The amount of coke is also found to increase with increase in Pd content of the catalysts. The highest amount of coke estimated, for instance, in the deactivated 20 wt% Pd catalyst is 7.3%. Nevertheless, these catalysts can be regenerated in air (at 250 °C for 2 h) and can be used again for more number of cycles with consistent performance. The comparison of catalytic performance of fresh and regenerated catalysts is shown below and discussed.

Some interesting observations can be made if we compare the influence of Pd loading (0.5–20 wt% Pd) shown in Fig. 3a and the Sb loading (4–20 wt%) presented in Fig. 2, in terms of activity enhancement effects vs. Pd particle size. In earlier investigations [12], it has been observed that both the catalytic activity and the Pd particle size were observed to increase continuously up to 20 wt% Pd. In contrast, with change in Sb loading, the activity and the size of Pd particles increased only up to 8 wt% Sb and then decreased with further increase [14]. One common aspect between these two systems is that the catalytic activity is changing in accordance with the changes in the Pd particle size. Therefore, one can conclude that the size of Pd particles has a clear influence on the catalytic performance and bigger particles are suitable for better performance. Though this phenomenon of increasing activity with increase in Pd particle size is somewhat unusual, there are reports in the literature [15–17] where the bigger Pd particles are more active than the smaller ones. The authors interpreted their results in terms of differences in the adsorption strength of reactant molecules over smaller and bigger Pd particles. The decrease in the catalytic activity with decrease in Pd particle size was also explained by the changes in the electronic structure of small Pd nanoparticles, leading to stronger interaction with the educts and further to easy deactivation. Similar such modifications can also be expected here in the present catalysts. Based on these results, it can be stated that more pronounced differences between the catalytic behaviour of very small and large Pd particles were clearly noticed.

3.5. Changes in the catalytic performance of 20Pd–8Sb/TiO_2 catalyst with time-on-stream

Time-on-stream behaviour of 20Pd–8Sb/TiO_2 is depicted in Fig. 3b. The figure clearly demonstrates that the catalyst display a very low initial activity (X-Tol = ∼3%), which is found to increase continuously with time reaching maximum approximately after 7 h giving maximum conversion of toluene (>90%) and then decrease noticeably with time. This increase in activity at around 7 h might be the time needed for the growth of Pd particles to a critical size to display such higher activity. It should be noted that all other catalysts of this series also showed similar such tendency of decreasing activity with time-on-stream. This observation supports the view that higher activity is associated with bigger Pd particles that are formed during the course of reaction only after a certain period of time. However, the catalytic activity is apparently unrelated to the BA selectivity, which is found to be independent of conversion of toluene.

As mentioned earlier, the major problem with these catalysts is deactivation due to coke deposits. XPS also provided some hints for such deactivation due to coke deposits, which in turn leads to the formation of undesired palladium species (i.e. Pd(δ^-)) and causes a loss of both Pd and Sb in the near-surface region and thus affects the catalytic performance. Nonetheless, the deactivated catalysts can be regenerated in air and can be used for more number of cycles with consistent performance. XPS showed the presence of three types of Pd species on the surface of the spent catalyst such as (i) Pd(0), (ii) Pd(Ox) and (iii) Pd(δ^-) (i.e. the species with a lower binding energy than Pd(0)). Formation of such Pd(δ^-) species is expected from the interaction between surface Pd species with the coke and their formation is believed to be responsible for catalyst deactivation. On the other hand, no significant differences in the size of Pd particles between highly active and deactivated samples could be seen from TEM analysis. The only difference between these two samples is considerable amount of coke deposition. This result clearly indicates that the deactivation is mainly due to coke deposition but not due to agglomeration of Pd particles, which in fact seemed to be favourable for better performance. Similar such tendency in loss of activity with time-on-stream is also observed with all other catalysts of this series.

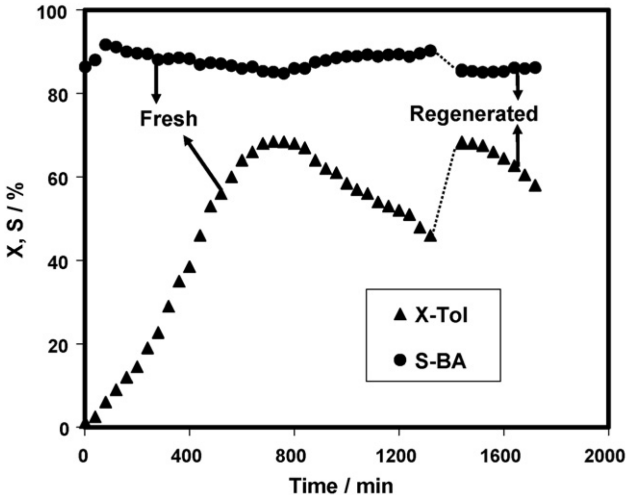

Fig. 4. Comparison of performance of fresh and regenerated 10Pd–8Sb/TiO_2 solid.

3.6. Comparison of catalytic performance of fresh and regenerated 10Pd–8Sb/TiO_2 catalyst

Comparison of performance of fresh and regenerated 10Pd–8Sb/TiO_2 solid is portrayed in Fig. 4. The dotted line in figure indicates the duration of regeneration time (2 h). It is obvious from the figure that the fresh catalyst is observed to exhibit very low initial activity (ca. 2%), which is increased further to a maximum of 68% after around 10 h, remained stable for another 3–4 h and then begins to decline with time, i.e. 46% after 22 h-on-stream. The tendency of changes in catalytic performance is observed to be very similar in all the catalysts of this series irrespective of Pd loading. It is evident that the deactivated catalyst after regeneration in air at 250 °C immediately restores its maximum activity that has been lost due to coking. This fact shows that the regeneration process effectively removes the coke from the catalyst surface. TEM analysis gave further evidence that such regeneration has no effect on the size of Pd particles as both the regenerated and deactivated solids contains Pd particles of similar type with comparable size. It can also be noticed from the activity curves that no significant changes between the fresh and regenerated catalysts particularly in the tendency of change of activity and selectivity behaviour with time-on-stream. In other words, both the fresh and regenerated catalysts exhibited conversion of toluene as high as 68% and benzyl acetate selectivity of ca. 85%. It is notable that the regenerated catalysts were found to display consistent performance for more number of cycles due to effective removal of coke from the catalyst surface.

3.7. Changes observed in the particle size of Pd (in 10Pd–8Sb/TiO_2 catalyst), coke deposition and conversion of toluene at different stages of reaction

After characterising less active fresh catalysts and deactivated used catalysts by various techniques, we understood that substantial changes are being occurred during the course of the reaction. Change in Pd particle size was one such important parameter, which has a great influence on the performance. In order to verify these ideas to the maximum possible extent, the work was then devoted to examine such changes particularly in the Pd particle size during the course of the reaction and its further influence on the catalytic performance. For this purpose, a 10Pd–8Sb/TiO_2 was selected as a model catalyst and subjected to different test runs covering different stages of reaction such as (i) activated, (ii) maximum active (11 h-on-stream), (iii) deactivated (22 h-on-stream), (iv) regenerated, etc. and then characterised by TEM.

Electron micrographs of 10% Pd–8% Sb/TiO_2 catalyst subjected to different stages of reaction are presented in Fig. 5. Careful examination of these results reveals some interesting features with regards to the changes occurred in terms of (i) Pd particle size, (ii) coke deposition and (iii) conversion of toluene. The denotations of these samples are described in the footnote of the figure caption. The first image (Fig. 5, image A) corresponds to an activated sample, in which the size of Pd particles is found to be considerably smaller (1–10 nm), which is however more or less similar to that of fresh catalyst. This result implies that the growth of Pd particle is not occurring during activation step. If we watch the next image, i.e. after 6 h of catalytic runs (Fig. 5, image B), where the conversion of toluene reached nearly 35%, the sample exhibited some bigger Pd particles. This result indicates that the growth of Pd particles is started during the course of reaction under the influence of reactant feed mixture. However, this sample contains mixture of both smaller (~2 nm) and bigger Pd particles (20 nm). More number of smaller Pd particles than bigger ones appear in this catalyst. At the same time, coke deposition also begins to occur at this stage and this sample contains 1.2% coke in it. In the next stage, the Pd particle size is further increased and reached maximum size around 80 nm (Fig. 5, image C) where the catalyst displayed the maximum activity (X-Tol = 68.5% after 11 h-on-stream). In other words, the conversion of toluene increased from 35 to 68% with increase in Pd particle size. This fact clearly demonstrates that the bigger Pd particles are favourable for better performance. The amount of coke also found to increase to 2.3%. The maximum activity is retained constant for another 3 h and started declining, however there is no such decrease in the Pd particle size. The catalyst even after testing for 18 h (Fig. 5, image D) exhibited more or less similar Pd particles as the previous one but lost its activity to a considerable extent. The conversion of toluene decreased from 68 to 57%, while the amount of coke is increased from 2.3 to 5.2%. This tendency of decrease in activity is continued with time-on-stream. After 22 h-on-stream (Fig. 5, image E), the conversion of toluene is further reduced to 46%, but there is absolutely no change in Pd particle size. However, the carbon deposition continued to increase up to 6.3%. This fact suggests that the decline in catalytic activity is mainly due to coke deposition but not due to increase in Pd particle size, which remained more or less constant from 11 h onwards. Interestingly, there is also no considerable difference in the Pd size between maximum active and deactivated sample. The only difference lies in the amount of coke deposition and hence the degree of conversion levels. Coming to the regenerated catalyst (Fig. 5, image F), after removal of coke, immediately exhibited similar activity as that of maximum active catalyst (X-Tol = 68%). Again, the Pd particle size is more or less similar to those of maximum active and deactivated samples. This observation undeniably supports the view that the catalytic performance is strongly dependent on Pd particle size and the larger particles are always favourable for better performance of the catalysts, which is also in good agreement with the literature reports [2]. It is also observed that the regeneration process is effective only in removal of coke deposits from the catalyst surface, but it has no effect on Pd particle size. Regenerated catalyst, though it contains 1.7% coke, it is capable of restoring the maximum activity that is lost during high coke deposition. This result implies that up to 2% coke deposition has no considerable detrimental effect on catalytic performance. Additionally, similar such increase in activity with increase in Pd particles is also commonly observed on various other Pd–M/TiO_2 catalysts (where M = Sb, Sn, Bi, Cu).

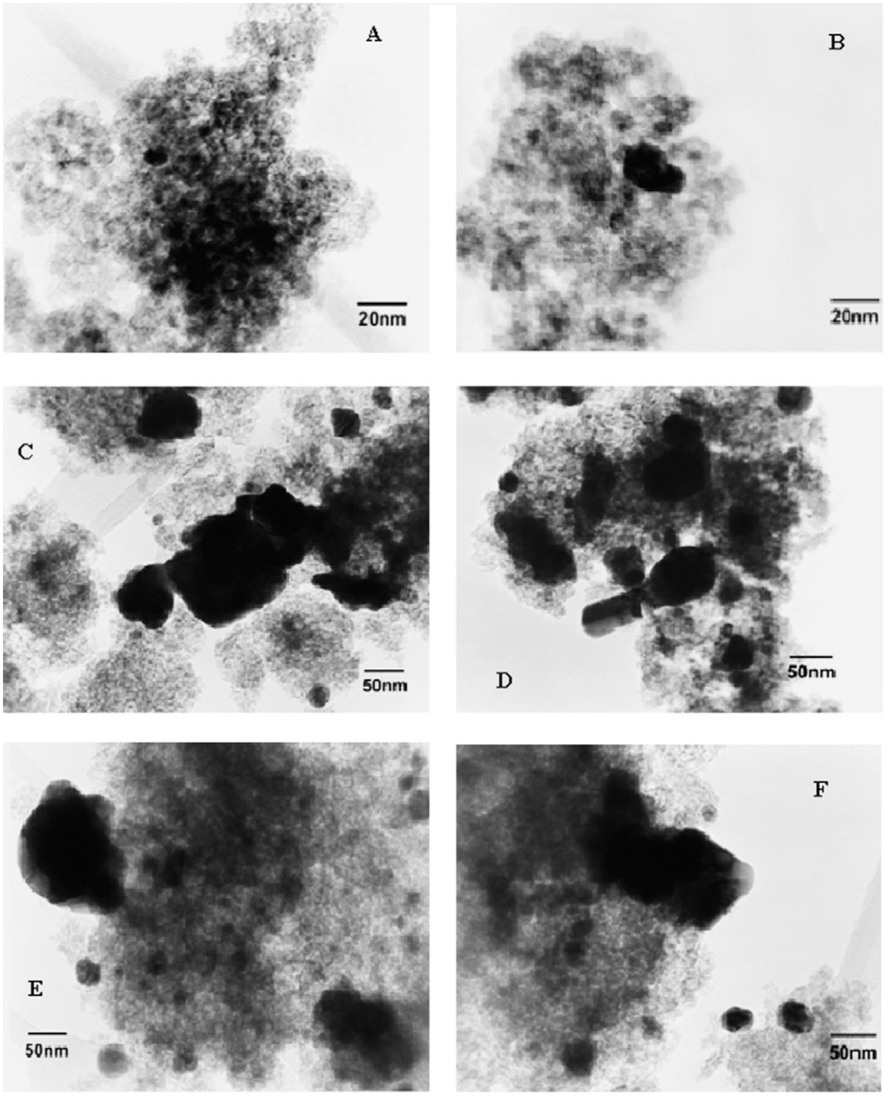

Fig. 5. Electron micrographs of 10Pd–8Sb–TiO_2 at different stages of reaction. (A) Activated sample, coke = 0.0%; (B) after 6 h-on-stream, X-Tol = 35%, coke = 1.2%; (C) after 11 h-on-stream, X-Tol = 68%, coke = 2.3%; (D) after 18 h-on-stream, X-Tol = 57%, coke = 5.2%; (E) after 22 h-on-stream, X-Tol = 46%, coke = 6.3%; (F) regenerated sample, X-Tol = 68%, coke = 1.7%.

3.8. Influence of support on the catalytic performance of 10Pd–8Sb acetoxylation catalysts

After testing the influence of Pd loading, Sb loading and time-on-stream behaviour of Pd–Sb/TiO_2 catalysts, the focus is then laid on investigating the influence of support on the catalytic performance. For this purpose, four different supports such as TiO_2, γ-Al_2O_3, SiO_2 and ZrO_2 are selected as suitable supports. The catalytic results obtained on the influence of support on the catalytic performance of Pd–Sb catalysts are presented in Fig. 6a. It is clear from the figure that the nature of support has a strong influence on the catalytic performance of the catalysts. TiO_2 (anatase)-supported Pd–Sb catalyst is observed to exhibit superior performance compared to all other supports. The highest conversion of toluene (X-Tol = 68%) and yield of BA (Y = 58%) was obtained over TiO_2 (anatase)-supported catalyst. The lowest activity and the highest CO_x (ca. 30%) were found on ZrO_2- and Al_2O_3-supported catalysts (X-Tol = ~10% and Y-BA = ~8%). In addition to the strong influence of the support on the catalytic performance, the size of Pd, which is very important in this reaction, is also found to vary with changing the support even though the Pd content kept constant at 10 wt% in all the catalysts. Furthermore, all these catalysts were observed to deactivate after several hours of operation and this deactivation is mainly due to coke deposition on the catalyst surface. Nevertheless, these catalysts can be regenerated in air at 250 °C for 2 h and can be used consistently for more number of cycles. The differences in the catalytic activity of these four supports can be ascribed to the differences in the size of Pd particles and acidity characteristics as both these parameters play a key role on performance. The better performance of TiO_2 support is due to formation of bigger Pd particles (80–100 nm) plus higher acidity of this catalyst compared to all other three supports.

- Decreasing order of Pd size: $TiO_2 > SiO_2 > ZrO_2 \sim Al_2O_3$.
- Decreasing order of activity: $TiO_2 > SiO_2 > ZrO_2 \sim Al_2O_3$.

3.9. Time-on-stream behaviour of 10Pd–8Sb catalysts with different supports

Variation of catalytic performance of Pd–Sb solids with time-on-stream is given in Fig. 6b. Though the tendency of increase in the conversion of toluene and the yield of BA are found to be more

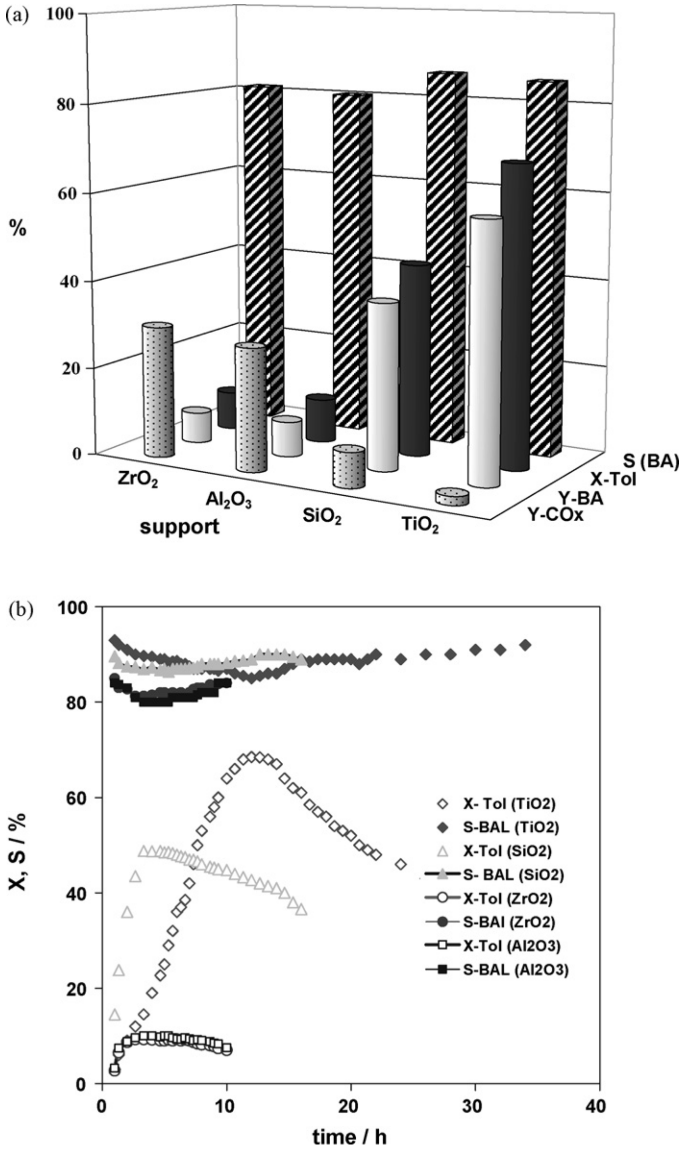

Fig. 6. (a) Influence of support on the catalytic performance of 10Pd–8Sb/S catalysts (S = ZrO_2, γ-Al_2O_3, SiO_2 and TiO_2). (b) Variation of catalytic performance of 10Pd–8Sb/S catalysts with time-on-stream (S = ZrO_2, γ-Al_2O_3, SiO_2 and TiO_2).

or less same in all the catalysts, there still exist certain differences particularly in the level of their performance. As mentioned earlier, TiO_2-supported solid displayed the best performance in view of its high Lewis acidity and bigger Pd particles, while the γ-Al_2O_3- and ZrO_2-supported solids gave the poor performance due to the presence of smaller Pd particles in them. On the other hand, the maximum conversion of acetic acid (>35%) was obtained over γ-Al_2O_3- and ZrO_2-supported ones, which is nearly four times higher than the conversion of toluene (9%) on the same solids. In a similar way, the yield of CO_x ($\geq$30%) obtained over these solids is also observed to be four times higher than the yield of BA (ca. 8%). This result clearly suggests that the formation of CO_x is occurring mainly from the decomposition of acetic acid but not from toluene. The conversion of toluene over 10Pd–8Sb/TiO_2 solid is increased from 3.5% at first hour to a maximum of 68.5% after ca. 10 h and then decreased to 30% after 34 h-on-stream. The variation in the yield of BA with time-on-stream is also found to change exactly in the same manner as that of conversion of toluene. It is noteworthy that the selectivity of BA is varied over a small range (S = 80–85%) irrespective of conversion and nature of support used.

Another difference lies in the time needed for attaining steady state conditions and to display maximum activity (ca. 3 h for Al_2O_3, ZrO_2 and SiO_2 while 10 h for TiO_2). It is reasonable to assume that the growth of Pd particle size to 100 nm (TiO_2) takes more time compared to the one growing only to 10 nm (Al_2O_3). Therefore, it is not quite surprising that the TiO_2-supported sample having the biggest Pd particles (ca. 100 nm) took longer time compared to others. Furthermore, the growth mechanism of Pd particles might also be different and may depend on the nature of support applied. As expected, γ-Al_2O_3- and ZrO_2-supported solids took only 3 h because of their small Pd particles (ca. 10 nm), but surprisingly even SiO_2-supported one though it contained some bigger Pd particles up to 60 nm took similar time. This result indicates that the process of Pd growth in SiO_2-supported catalyst is either faster or follows different growth mechanism.

3.10. Influence of Pd loading on the acetoxylation of toluene over Pd–8Sb–7Bi/TiO_2 catalysts

After a detailed study on the influence of Pd loading on the acetoxylation activity and selectivity behaviour of the earlier Pd–Sb/TiO_2 catalysts, we have reached respectable yields of benzyl acetate close to 80% and conversion of toluene over 90%, but yet we could not overcome the problem of catalyst deactivation. In an attempt to overcome such deactivation problem, attempts were made to modify catalyst composition with suitable promoters. Addition of Bi to Pd–Sb solids is one such successful example in enhancing the long-term stability. Afterwards, our research efforts were further extended to explore Pd–Sb–Bi composition with varying Pd contents over a broad range (0.5–20 wt%) while keeping Sb and Bi at 8 and 7 wt%, respectively.

Fig. 7a illustrates that an increase in Pd loading has an accelerating effect on the catalytic performance of Bi modified catalysts similar to earlier Pd–Sb solids. The conversion of toluene has been increased dramatically from 10 to 71% with increase in Pd loading from 0.5 to 20 wt%. Increase in conversion of toluene has no significant effect on the selectivity of BA, which remained more or less constant at around 95%. Therefore, the yield of BA is increased from ~10% to 67.5% with increase in Pd loading. Again, BAL is the major by-product and the balance is CO_x. An interesting effect exercised by the addition of Bi is not only achieving extremely high selectivity of benzyl acetate (S = $\geq$95%) but also improved long-term stability of the catalysts. 10Pd–8Sb–7Bi/TiO_2 solid was tested up to 160 h and no loss of activity and selectivity over such a long period is noticed. The origin of promoting role of Bi on the catalyst life and BA selectivity might be due to weakening of interaction between coke and surface Pd species, which in turn prevents the formation of the so-called Pd(δ^-) species [18]. On the other hand, if we compare the performance of the present Bi-containing catalysts with that of earlier Pd–Sb/TiO_2 catalysts shown in Fig. 3b (i.e. in absence of Bi), the tendency of changes in activity and selectivity (BA and BAL) are very much comparable. The main difference however lies in the long-term stability. Comparing these two results, it can be inferred that an increase in Pd content has a promotional effect on the activity of the catalysts. The result clearly indicates that the combination of Pd, Sb and Bi successfully improves the activity, selectivity and lifetime of the catalysts. Additionally, Pd–Sb used samples (in absence of Bi) exhibited somewhat higher coke (up to 7% in about 30 h-on-stream) compared to Bi-containing catalysts ($\leq$5% coke after 100 h-on-stream). In spite of ca. 5% coke in Bi-containing catalysts, they did not show any deactivation because the presence of Bi suppress the interaction between the coke and surface Pd species.

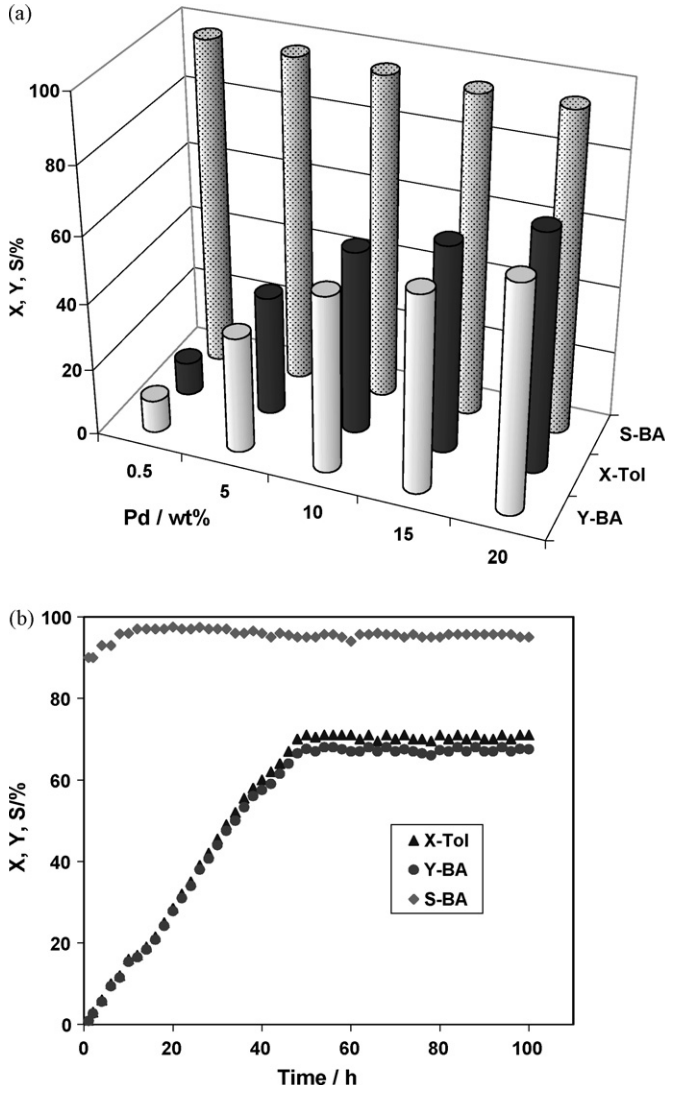

Fig. 7. (a) Influence of Pd loading on the catalytic performance of Pd–8Sb–7Bi/TiO_2 catalysts. (b) Variation of catalytic performance of 20Pd–8Sb–7Bi/TiO_2 with time-on-stream.

There is corroborative evidence from XPS [18] that the presence of Bi has a significant influence on weakening the interaction between the surface Pd species and carbon atoms from coke deposits, which ultimately prevent the formation of Pd(δ^-) species, which seem to be responsible for the catalyst deactivation. On the whole, it can be stated that the combination of Pd–Sb–Bi improved both the long-term stability and the desired product selectivity.

3.11. *Time-on-stream behaviour of 20Pd–8Sb–7Bi/TiO_2 catalyst*

It can be seen from Fig. 7b that the catalyst requires nearly 2 days two display maximum activity and this seems to be the time needed for the growth of Pd particles to a critical size (ca. 80–100 nm) that is necessary for better performance. From 50 h onwards there is no deactivation for a period of 100 h as tested in our laboratory. The catalyst exhibited very low initial activity, which is found to increase progressively up to 50 h and reaching maximum activity at around 71% and then display quite consistent performance through out. However, the selectivity of BA remained more or less constant around 95% through out (i.e. for a period of 100 h). Additionally, if we compare the performance of this catalyst with that of Pd–Sb/TiO_2 (i.e. in absence of Bi) with identical amount of Pd (20 wt%) in it, the behaviour of these two catalysts is found to be considerably different in terms of catalytic activity and long-term stability. In absence of Bi, the catalyst displayed very high activity (over 90%) but easy deactivation with time-on-stream (ca. 10 h). However, the addition of Bi reduced the catalyst activity to a certain extent, but enormously enhanced the lifetime as well as the selectivity of the target product, benzyl acetate. The major difference is that Bi modified catalysts are usually taking much longer time to attain steady state compared non Bi-containing catalysts. This fact suggests that the growth mechanism of Pd in presence of Bi might be either slow or following another growth mechanism than that of only Pd–Sb solids (i.e. in absence of Bi). Again, BAL is the main by-product but with relatively low selectivity ($\leq$5%).

4. Conclusions

Combination of Sb and Pd in Pd–Sb/TiO_2 enhanced (i) the catalytic activity, (ii) selectivity and (iii) suppressed the formation of CO_x. Activity increased with increase in Pd loading. The loss of Pd and Sb in the near-surface region due to coke deposits and the formation of Pd(δ^-) species during the reaction are believed to be the reasons for the observed catalyst deactivation. Comparison of dependencies of Pd particle size and the catalytic activity, it is obvious that the activity is increased basically in the same manner as that of Pd particle size. Apparently Pd surface atoms on larger particles seem to be more active than those on smaller ones. Bi modification of Pd–Sb solids not only solved the problem of catalyst deactivation but also enhanced the selectivity of benzyl acetate up to 95%. This is indeed a good achievement and remarkable outcome of this study.

References

[1] S.K. Tanielyan, R.L. Augustine, J. Mol. Catal. 87 (1994) 311.
[2] E. Benazzi, C.J. Cameron, J. Mol. Catal. 69 (1991) 299.
[3] M.S. Chen, K. Luo, T. Wei, Z. Yan, D. Kumar, C.-W. Yi, D.W. Goodman, Catal. Today 117 (2006) 37.
[4] J.-R. Chen, C.-M. Lee, Proc. Safety Prog. 24 (2005) 280.
[5] L. Eberson, L. Jönsson, Acta Chem. Scand. B 28 (1974) 597.
[6] T. Miyake, A. Hattori, M. Hanaya, S. Tokumura, H. Hamaji, T. Okada, Top. Catal. 13 (2000) 243.
[7] T. Komatsu, K. Inaba, T. Uezno, A. Onda, T. Yashima, Appl. Catal. A 251 (2003) 315.
[8] M. Martin, G. Scharfe, G. Wolfgang, DE 2,107,913 (1971) (Bayer AG, Germany).
[9] T. Onoda, K. Wada, US 4,033,999 (1977) (Mitshubishi Chem. Ind. Ltd., Tokyo, Japan).
[10] A. Benhmid, K.V. Narayana, A. Martin, B. Lücke, Chem. Commun. (2004) 211.
[11] A. Benhmid, A. Martin, V.N. Kalevaru, B. Lücke, S. Bischoff, WO 2005/066107 A1 (2005) (Tessenderlo Chemie S.A., Belgium).
[12] A. Benhmid, K.V. Narayana, A. Martin, B. Lücke, S. Bischoff, M.-M. Pohl, J. Radnik, M. Schneider, J. Catal. 230 (2005) 420.
[13] H. Shinohara, Appl. Catal. 10 (1984) 27.
[14] V.N. Kalevaru, A. Benhmid, J. Radnik, B. Lücke, A. Martin, J. Catal. 243 (2006) 25.
[15] S. Hub, L. Hilaire, R. Touroude, Appl. Catal. 36 (1988) 307.
[16] B. Tardy, C. Noupa, C. Leclercq, J.C. Bertolini, A. Hoareau, M. Treilleux, J.P. Faure, G. Nihoul, J. Catal. 129 (1991) 1.
[17] J.C. Bertolini, P. Delichere, B. Khanra, J. Massardier, C. Noupa, B. Tardy, Catal. Lett. 6 (1990) 215.
[18] J. Radnik, A. Benhmid, V.N. Kalevaru, M.-M. Pohl, A. Martin, B. Lücke, U. Dingerdissen, Angew. Chem. Int. Ed. 44 (2005) 6771.