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Catalysis Today 112 (2006) 192–196

CATALYSIS TODAY

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Direct synthesis of benzyl acetate and optimisation of reaction conditions for the gas phase acetoxylation of toluene

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Abstract

TiO_2 supported Pd-Sb catalysts were prepared by impregnation method and tested for the selective vapour phase acetoxylation of toluene to benzyl acetate (BA). Investigations were carried out to optimise reaction variables such as effects of reaction temperature, acetic acid/toluene mole ratio, O_2/toluene mole ratio, contact time, etc. to obtain better performance of the catalysts. Additionally, the influence of Sb/Pd ratio on catalytic performance was also checked under optimised reaction conditions. The activity of the catalysts was found to increase continuously with increasing Sb/Pd ratio up to 0.7 and then decreased with further increase in Sb/Pd ratio to 1.75. The catalyst with Sb/Pd ratio of 0.7 exhibited the best performance among all other catalysts of this series giving a conversion of toluene as high as ca. 68% with BA selectivity of 85%. All these catalysts were observed to deactivate with time on stream due to considerable amount of coke deposition. However, these catalysts can be regenerated in air and reused for more number of cycles with consistent performance.

Keywords: Gas phase acetoxylation; Toluene; Sb-Pd/TiO_2 catalysts; Optimization of process parameters; Sb/Pd ratio

1. Introduction

The direct partial oxidation of methyl aromatics to their corresponding aldehydes or alcohols is often unselective as the desired products undergo further oxidation. Therefore, these oxidation reactions rather continue to yield more thermodynamically stable end products, for instance benzoic acid from toluene [1]. Therefore, an important challenge for the future is to develop more attractive processes/effective catalysts to obtain the desired compounds as stable end products. This problem may be solved to a considerable extent if the selective oxidation is carried out using suitable catalysts and appropriate auxiliary reagents. Acetoxylation of methyl aromatics to produce benzyl esters in a single step is one such good example for preventing over-oxidations and producing stable target products, which are resistant to further oxidation.

Literature survey reveals that the acetoxylation of ethylene [2], propylene [3] and butadiene [4,5] are well-known processes and commercialised several years ago. In addition, various research groups also investigated acetoxylation of toluene over Pd based catalysts e.g. [6–9]. However, no catalyst was successful till date for commercialisation of this reaction. Most of the work reported so far was carried out under liquid phase conditions [6–11]. The literature reports on gas phase acetoxylation of toluene are very rare [12,13] on the one hand and on the other hand no considerable success has been achieved so far in terms of achieving higher benzyl acetate (BA) yields. From the state of the art, it is known that vapour phase acetoxylation is still under developmental stage and hence only a limited data available.

The vapour phase acetoxylation of toluene, in particular, is of great interest from both academic as well as industrial viewpoints as the target product BA is widely used in perfumery, food and chemical industries. We have reported earlier the superior performance of Pd-Sb/TiO_2 catalysts with different Pd loadings for the selective gas phase acetoxylation of toluene [14,15]. However, the catalyst deactivation still remained unsolved over these catalysts. In another study, we have also successfully solved the deactivation problem by

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[1] A member of the EU-funded Coordination Action of Nanostructured Catalytic Oxide Research and Development in Europe (CONCORDE).

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doi:10.1016/j.cattod.2005.11.041

suitable modification of catalysts by the addition of different promoters [16,17].

With this background, the present study is taken up to optimise the reaction conditions for enhancing the activity and selectivity behaviour of the catalysts. The intention is also to investigate especially the influence of Sb/Pd ratio on the acetoxylation activity of Sb-Pd/TiO_2 catalysts.

2. Experimental

2.1. Catalyst preparation

Different Sb-Pd/TiO_2 catalysts with constant Pd (10 wt%) and varying Sb contents in order to vary Sb/Pd ratios have been prepared by wet impregnation technique as described elsewhere [14–18]. Additionally, two other catalysts (8% Sb-5% Pd/TiO_2 and 8% Sb-5% Pd/SiO_2) were also prepared in a similar way. These two catalysts were used to optimise various reaction parameters.

2.2. Activity measurements

The catalytic tests were carried out in a fixed bed stainless steel reactor. One milliliter of catalyst is loaded in the reactor and the reaction is performed at 2 bar. The catalyst was activated in situ under airflow at 300 °C for 2 h prior to the activity tests. The organic feed mixture of toluene and acetic acid was pumped to the reactor using a HPLC pump. The product stream was analysed on line by GC [15].

3. Results and discussion

3.1. Characterisation of the catalysts

BET surface areas and pore volumes of Sb-Pd/TiO_2 catalysts with different Sb/Pd ratios are observed to decrease from 96 to 39 m^2/g and 0.164 to 0.058 cm^3/g, respectively, with increasing Sb/Pd ratio from 0.35 to 1.75. XRD patterns of the fresh catalysts up to Sb/Pd ratio of 1.05 showed only reflections corresponding to PdO and TiO_2 (anatase). Nevertheless, in the catalysts with higher Sb/Pd ratios, reflections that correspond to $NaSb(OH)_6$ and $HSbO_3{\cdot}(H_2O)_{0.27}$ are also identified in addition to PdO and TiO_2. XRD patterns of used catalysts are found to be considerably different from those of fresh catalysts. It is interesting to note that the used catalysts showed intense reflections that correspond to both metallic Pd and PdO phases, which is a clear indication of strong sintering. This observation lent good support to the observations made from TEM that the catalysts underwent drastic changes during the course of the reaction. TEM analysis of these catalysts also revealed that the presence of Sb has a strong influence on increasing the size of Pd particles. The size of Pd particles in some of the used catalysts was grown even up to 90 nm compared to their corresponding fresh catalysts, in which the Pd particle size was only <10 nm. This increase in particle size can be attributed to the agglomeration process occurring during the course of reaction.

3.2. Catalytic activity

3.2.1. Optimisation of reaction conditions

In view of significant number of variables, extensive testing of the acetoxylation of toluene was carried out during initial stages of work over supported Sb-Pd catalysts in order to obtain first approximation of the conditions required for the reaction. The different reaction variables that are expected to have significant influence on the catalytic performance of the catalysts are (i) reaction temperature, (ii) acetic acid/toluene mole ratio, (iii) O_2/toluene mole ratio, and (iv) contact time. The results on the influence of all these process parameters, which revealed very interesting results, are discussed below in more detail.

3.2.1.1. Influence of reaction temperature on the acetoxylation activity of 8% Sb-5% Pd/TiO_2 catalyst. Influence of reaction temperature on the catalytic performance is illustrated in Fig. 1. It is evident from that the temperature has a promotional effect on the conversion of toluene as well as the BA yield, which have increased from 27 to 47% and 24 to 39%, respectively, with increase in temperature from 175 to 250 °C. The selectivity of BA is marginally decreased from 88 to 83%, while the yield of benzaldehyde that is formed as by-product is increased from 3 to 8% with rise in temperature. The formation of CO_x was found to increase at a slower rate up to 210 °C and then raised sharply from 5 to ca. 18% with further increase in temperature to 250 °C. It has been shown earlier [15] that the formation of CO_x is mainly occurring from the oxidative decomposition of acetic acid but not from toluene. In view of such higher decomposition of acetic acid and high amounts of CO_x formation beyond 210 °C [15], the reaction temperature of 210 °C has been selected as an optimum and used in further

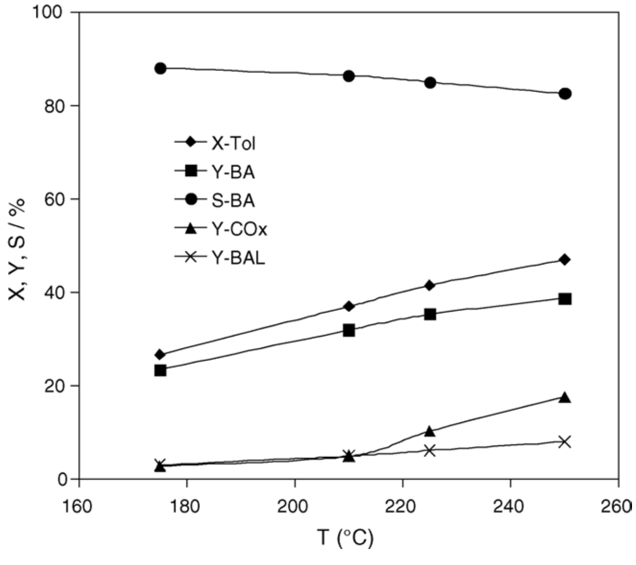

Fig. 1. Influence of reaction temperature on the catalytic performance of 8% Sb-5% Pd/TiO_2 catalyst (GHSV (STP) = 2688 h^{-1}; τ = 1.34 s; mole ratio of toluene:acetic acid:O_2:IG (inert gas) = 1:4:3:16; X-Tol: conversion of toluene; Y-BA: yield of benzyl acetate; S-BA: selectivity of benzyl acetate; Y-CO_x: yield of carbon oxides; Y-BAL: yield of benzaldehyde).

catalytic tests though it displays slightly low conversion of toluene compared to 250 °C.

This kind of oxidative decomposition is also evidenced from present experiments that significant increase of acetic acid conversion from 26 to 56% with increase in temperature from 175 to 250 °C. The reaction was performed at a GHSV = 2688 h^{-1}; residence time = 1.34 s; and a mole ratio of toluene:acetic acid:O_2:IG (inert gas) = 1:4:3:16.

3.2.1.2. Influence of acetic acid to toluene mole ratio on the acetoxylation activity of 8% Sb-5% Pd/TiO_2 catalyst. A study on acetic acid/toluene mole ratio on the catalytic performance of 8% Sb-5% Pd/TiO_2 catalyst was carried out with a view to identify the optimum mole ratio. It is clear from Fig. 2 that both the conversion of toluene and the yield of BA are observed to increase from 24 to 37% and 19 to 32% with increase in acetic acid to toluene mole ratio up to 4 and then remained more or less constant with further increase. The conversion of acetic acid is also found to increase from 32 to 37% with increase in the concentration of acetic acid.

It is noteworthy that the yields of carbon oxides were drastically decreased from 13 to 5% with increase in acetic acid/toluene mole ratio up to 4 and then remained unaltered beyond this ratio. This result indicates that the oxidative decomposition of acetic acid is considerably reduced with increased concentrations of acetic acid in the reactant feed gas and directed the reaction in a desired route. The selectivity of BA is increased marginally from 80 to 86% while the yield of benzaldehyde remained almost constant (ca. 5%) through out the acetic acid/toluene molar ratio used in the present study. According to Shinohara [5], the conversion of butadiene increased with increase in the partial pressure of acetic acid in the gas phase acetoxylation of 1,3-butadiene over Sb-Pd-KOAc catalyst. From these results, we found that acetic acid to toluene mole ratio of 4 is optimum for getting maximum yield of BA with less amounts of CO_x.

3.2.1.3. Influence of oxygen to toluene mole ratio on the acetoxylation activity of 8% Sb-5% Pd/SiO_2 catalyst. After optimising acetic acid/toluene mole ratio, the influence of O_2/toluene mole ratio has been investigated under the similar reaction conditions as those used for previous tests. Fig. 3 depicts that the conversion of toluene and yield of BA are observed to increase continuously from 10 to 32% and 8.5 to 28%, respectively, with increase in O_2/toluene mole ratio up to 3 and then decreased slightly with further increase in oxygen concentration in the feed gas.

It is interesting to note that a rise in O_2/toluene mole ratio from 0.5 to 3.5 caused an enormous increase (ca. three times) in the yields of CO_x (from 2.3 to 7.8%) and the conversion of acetic acid from ca. 10 to 30%. This result clearly indicates that higher oxygen concentration in the feed gas has an adverse effect and enhances the oxidative decomposition of acetic acid leading to the formation of higher amounts of CO_x. However, no considerable change in the selectivity of BA is observed, which remained more or less stable at around 85%. The yield of benzaldehyde is varied over a small range from 2 to 4%. Maximum acetoxylation activity is observed to occur at O_2/toluene mole ratio of 3 and hence this parameter is used in further catalytic tests.

3.2.1.4. Influence of contact time on the acetoxylation activity of 8% Sb-5% Pd/TiO_2 catalyst. Effect of contact time on the catalytic performance is shown in Fig. 4. It is quite interesting to note that the conversion of both toluene and acetic acid was observed to become double (i.e. from 21 to 40%) with increase in contact time from 0.47 to 1.61 s. The BA yield is also found to increase continuously from 19 to 35% with increase in contact time. However, there is not much considerable influence of contact time on the BA selectivity as well as the yield of benzaldehyde, which were varied over a small range from 86 to 89% and 2.5 to 5%, respectively. The yield of CO_x

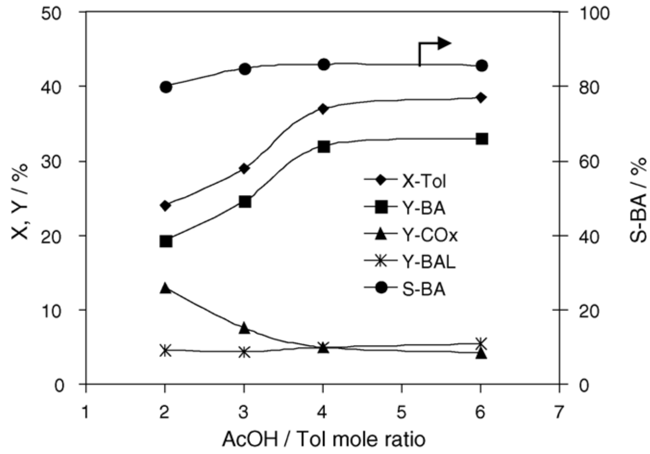

Fig. 2. Influence of acetic acid to toluene mole ratio on the catalytic performance 8% Sb-5% Pd/TiO_2 catalyst ($T = 210$ °C; GHSV (STP) = 2688 h^{-1}; $\tau = 1.34$ s; mole ratio of toluene: acetic acid:O_2:IG (inert gas) = 1:3:14:18; X-Tol: conversion of toluene; Y-BA: yield of benzyl acetate; S-BA: selectivity of benzyl acetate; Y-CO_x: yield of carbon oxides; Y-BAL: yield of benzaldehyde).

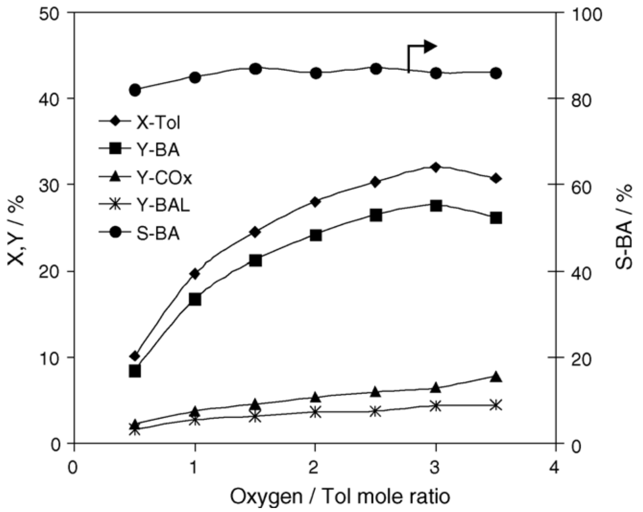

Fig. 3. Influence of oxygen to toluene mole ratio on the catalytic performance 8% Sb-5% Pd/SiO_2 catalyst ($T = 210$ °C; GHSV (STP) = 2688 h^{-1}; $\tau = 1.34$ s; mole ratio of toluene:acetic acid:O_2:IG (inert gas) = 1:4:15.5:18.5; X-Tol: conversion of toluene; Y-BA: yield of benzyl acetate; S-BA: selectivity of benzyl acetate; Y-CO_x: yield of carbon oxides; Y-BAL: yield of benzaldehyde).

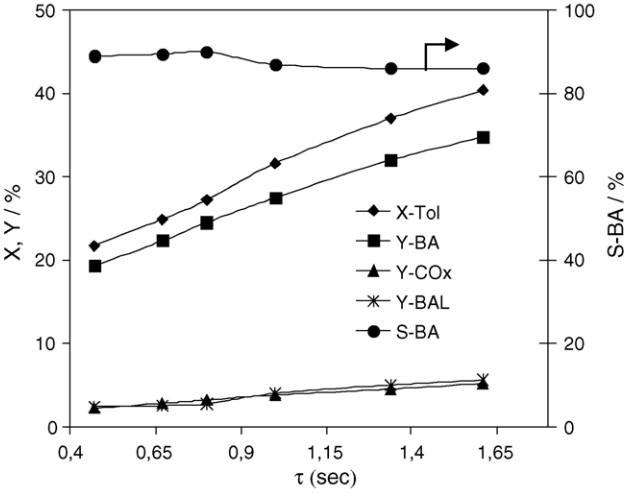

Fig. 4. Influence of contact time on the catalytic performance 8% Sb-5% Pd/TiO_2 catalyst ($T = 210$ °C; mole ratio of toluene:acetic acid:O_2:IG (inert gas) = 1:4:3:16; X-Tol: conversion of toluene; Y-BA: yield of benzyl acetate; S-BA: selectivity of benzyl acetate; Y-CO_x: yield of carbon oxides; Y-BAL: yield of benzaldehyde).

was increased continuously from ca. 2 to 5% with increase in contact time. From these results, a contact time of 1.34 has been chosen as an optimum and used in further catalytic tests.

3.2.2. *Influence of Sb/Pd ratio on the acetoxylation activity of Sb-(10%) Pd/TiO_2 catalysts*

Fig. 5 demonstrates that the conversion of toluene was increased from 30 to 68% with increasing Sb/Pd ratio from 0.35 to 0.7 and then decreased to 54% with further increase in Sb/Pd ratio to 1.75. The tendency of change of BA and benzaldehyde yields was also observed to be exactly similar as that of conversion of toluene. However, the selectivity of BA is found to remain unchanged (ca. 86%) regardless of Sb/Pd ratio. It is worthwhile to comment that the yield of CO_x remarkably decreased from 22 to 2% with increase in Sb/Pd ratio up to 0.7 and then remained almost constant at this level with further increase in Sb/Pd ratio to 1.75. This drastic decrease in the amounts of CO_x with increase in Sb content can be attributed to suppression of oxidative decomposition of acetic acid. Similar such phenomenon was also observed in our earlier investigations on gas phase acetoxylation of toluene [15].

Benazzi and Cameron [8] investigated the influence of Sn/Pd ratio on liquid phase acetoxylation of toluene and reported that the activity was continuously increased from ca. 10 to over 90% with increase in Sn/Pd ratio from 1 to 5 and then decreased with further increase in Sn/Pd ratio. Tanielyan and Augustine [10] showed in their study on liquid phase acetoxylation of toluene that at lower Sn/Pd ratios (<2), the catalyst behaviour was unstable and dissolution of palladium into the liquid phase (medium) was noticed. The authors also reported that higher Sn/Pd ratio (>2) improves the stability of the surface complexes and at the same time the presence of the excess Sn decreases the coordinative unsaturation of the Pd atoms and thus lowers their catalytic activity. Another study by Shinohara [5], on the influence of Sb/Pd ratio for the gas phase acetoxylation of 1,3 butadiene over Pd-Sb-KOAC catalysts, reported that the activity was increased up to Sb/Pd ratio of 0.4 and then lowered rapidly with further increase (ca. 2.5). He claimed that Pd and Sb are getting interacted with each other on Pd-Sb-KOAc catalyst and this interaction led to the improvement of both the activity and selectivity behaviour. He also reported that excess loading of Sb causes the lowering of the activity by covering the active species. Our results are in agreement with those reported in the literature that the addition of second metal has an appreciable influence on the catalytic performance.

However, these catalysts with different Sb/Pd ratios are observed to undergo deactivation with time on stream due to coke deposits during the course of the reaction. The amount of coke deposition in the used catalysts is shown in Table 1. It is clear from the results shown in Table 1 that the amount of coke is observed to increase with increase in the duration of the catalytic tests. The highest coke up to 6.3% was observed in the catalyst (Sb/Pd ratio = 0.7) that was tested for longer period of time (34 h). However, this catalyst exhibited the better performance compared to all other catalysts applied in the present study. The amount of coke is found to vary in the range from 3 to 5% in the catalysts tested between 15 and 20 h on stream.

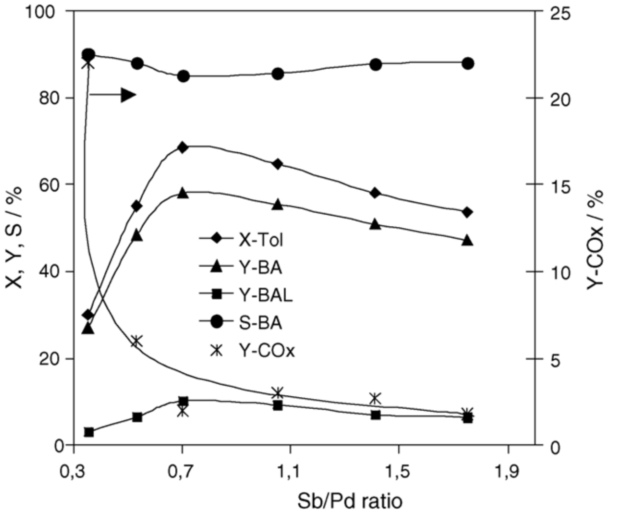

Fig. 5. Influence of Sb/Pd molar ratio on the catalytic performance Sb-Pd/TiO_2 catalysts ($T = 210$ °C; GHSV (STP) = 2688 h^{-1}; $\tau = 1.34$ s; mole ratio of toluene: acetic acid:O_2:IG (inert gas) = 1:4:3:16; X-Tol = conversion of toluene; Y-BA: yield of benzyl acetate; S-BA: selectivity of benzyl acetate; Y-CO_x: yield of carbon oxides; Y-BAL: yield of benzaldehyde).

Table 1
Influence of reaction period on coke deposits in the spent Sb-Pd/TiO_2 catalysts with different Sb/Pd ratios

Sb/Pd ratio	Coke (%)	Duration of tests (h)
0.35	4.8	15
0.70	6.3	34
1.41	3.9	18
1.75	3.2	20

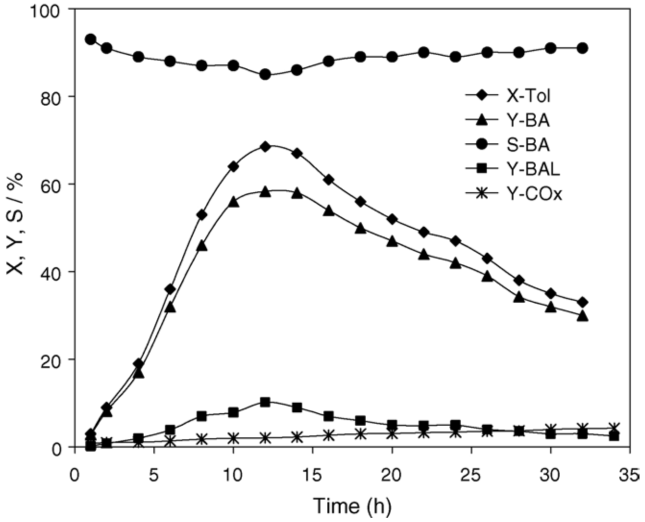

Fig. 6. Dynamic behaviour of Sb-Pd/TiO_2 catalyst during time on stream of gas phase acetoxylation of toluene ($T = 210\,^{\circ}C$; GHSV (STP) = 2688 h^{-1}; $\tau = 1.34$ s; mole ratio of toluene: acetic acid:O_2:IG (inert gas) = 1:4:3:16; X-Tol: conversion of toluene; Y-BA: yield of benzyl acetate; S-BA: selectivity of benzyl acetate; Y-CO_x: yield of carbon oxides; Y-BAL: yield of benzaldehyde).

3.2.3. Dynamic behaviour of Sb-Pd/TiO_2 catalyst (Sb/Pd = 0.7) during time on stream study of gas phase acetoxylation of toluene

The influence of dynamic behaviour of Sb-Pd/TiO_2 (Sb/Pd = 0.7) catalyst during working conditions on the catalytic performance is shown in Fig. 6. It is evident from the figure that the conversion of toluene is observed to increase continuously with time to a certain level and then decrease with further increase in the reaction time. In other words, the catalyst displayed very low initial activity (X-Tol = 3%), which is increased to 68% after ca. 10 h and then declined to 30% after 34 h on stream. Such tendency of catalytic behaviour is in line with the changes in the size of Pd particles during the course of the reaction. The fresh catalyst contained only smaller Pd particles (1–10 nm) and the size of which is found to increase continuously with time and reached maximum (ca. 80–100 nm) after ca. 10 h on stream, where the catalyst displayed maximum activity. This observation shows the dynamic behaviour of the catalyst and the promotional effect of Pd particle growth on the catalytic performance. Nevertheless, the catalytic activity is observed to decrease after about 14 h even though no such decrease in the Pd particle size is observed. Another interesting observation is that the coke deposition is also found to increase with time and reached maximum (6.3%) in this catalyst after 34 h on stream (Table 1). Therefore, such decrease in catalytic activity can be attributed to increased coke deposition during the course of the reaction rather than particle agglomeration. Similar such results on the amounts of coke deposition in the used catalysts, change of Pd particle size at different stages of reaction and their possible influence on the catalytic performance of the Pd-Sb catalysts with different Pd loadings are reported earlier [15]. The yield of benzyl acetate is also changed in a similar fashion as that of conversion of toluene. Additionally, formation of smaller amounts of benzaldehyde and CO_x were also observed as by-products of the reaction.

4. Conclusions

The Sb/Pd ratio is found to be one of the key parameters in governing the catalytic performance of the catalysts used. The presence of Sb has a significant influence on the growth of Pd particles. Spent catalysts exhibited much bigger Pd particles compared to their corresponding fresh catalysts. The reaction temperature of 210 °C, acetic acid to toluene mole ratio of 4, oxygen to toluene mole ratio of 3 and the contact time of 1.34 s were found to be optimum to obtain best catalyst performance.

Acknowledgements

Authors like to thank Dr. M. Schneider, Dr. J. Radnik, Mrs. Klinger and Mrs. Winkler for their help.

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