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Development of highly active and selective novel Pd based acetoxylation catalysts and prevention of catalyst deactivation by Bi modification†

A. Benhmid, K. V. Narayana, A. Martin,* B. Lücke and M.-M. Pohl
Institut für Angewandte Chemie Berlin-Adlershof e. V.‡, Richard-Willstätter-Str. 12, D-12489 Berlin, Germany. E-mail: a.martin@aca-berlin.de; Fax: +49-30-63 92 44 54; Tel: +49-30-63 92 43 06

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A first approach to successful prevention of catalyst deactivation while simultaneously achieving extremely high selectivity of benzyl acetate ($\geqslant$ 95%) at significantly high toluene conversion ($>$ 70%) by gas phase acetoxylation over novel Pd–Sb–Bi/TiO_2 catalysts.

Vapour phase acetoxylation of toluene, which is still at the developmental stage, is an interesting research field from both the academic and industrial viewpoints. The desired product, benzyl acetate (BA), is widely used in the fine chemical industry. Most of the studies reported so far on the direct synthesis of BA from toluene acetoxylation are confined to batch reactors in the liquid phase, *e.g.*[1–3] Only a few reports have appeared so far in the literature on gas phase acetoxylation of toluene.[4,5] However, no apparent success has been achieved to date in terms of obtaining higher yields of BA with longer life of the catalyst.[6,7] Recently, we have reported higher yields of BA, up to 78%, but the problem of deactivation still remained unsolved.[8] An attempt by Miyake *et al.*[9] to overcome catalyst deactivation using Pd–Bi catalyst (Pd : Bi = 3) in the liquid phase resulted only in 10% conversion of toluene.

Herein, we report a very attractive method for the direct synthesis of BA from toluene by gas phase acetoxylation. The primary aim of this study is to develop highly active and selective Pd based acetoxylation catalysts with improved catalyst life by suitable modification. Our intention is also to investigate the influence of Pd loading as well as time-on-stream behaviour of the best catalyst.

Two types of catalysts ((i) Pd–Bi/TiO_2 and (ii) Pd–Sb–Bi/TiO_2) are prepared by impregnation in two steps. (i) Pd–Bi/TiO_2 catalysts are prepared by impregnation of $BiCl_3$ on titania (anatase) carrier followed by oven drying (120 °C, 16 h) and further calcination at 400 °C (3 h, air). Then $PdCl_2$ is impregnated in the next step. In these catalysts the Pd : Bi ratio is varied in the range from 0.1 to 0.7 (with fixed Pd amount of 10 wt%). (ii) Pd–Sb–Bi/TiO_2 catalysts are prepared by impregnating $SbCl_3$ followed by $BiCl_3$ on anatase carrier with subsequent removal of excess solvent, drying of the solid and then calcination at 400 °C (3 h, air). The second step involves the impregnation of $PdCl_2$ to the above solid in desired amounts followed by drying (120 °C, 16 h). The content of Pd is varied over a wide range from 0.5 to 20 wt%, while the Sb and Bi are kept constant at 8 and 7 wt%. A detailed description of the catalyst preparation is given elsewhere.[10]

The catalytic tests were carried out in a fixed bed stainless steel reactor. 1 ml of catalyst is loaded in the reactor and the reaction is performed in presence of air at 210 °C and at 2 bars. 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 in the molar ratio of 1 : 4 was pumped to the reactor using an HPLC pump. The product stream was analysed online by GC.

With an increase in Pd loading from 0.5 to 20 wt% the surface areas and pore volumes were observed to decrease from 147 to 22 m^2 g^{-1} and from 0.204 to 0.036 cm^3 g^{-1}, respectively. XRD results showed the presence of BiOCl, Pd_2OCl_2 phases in the fresh catalysts of the second type. However, in the activated and used catalysts the Cl^- ions are totally removed and the presence of Pd and PdO has been noticed. TEM analysis of fresh 10% Pd–Bi/TiO_2 catalyst (Pd : Bi = 0.35) revealed that no titania in the surroundings of Bi can be seen. Bi exhibited sheet like morphology in the fresh catalysts. Small Pd particles in the range from $\sim$2 nm to 5 nm were found in the fresh catalysts even with 20% Pd catalyst. Pd, Sb, and TiO_2 are located in close proximity, while Bi is located far from TiO_2. No significant changes in Pd particle size are observed between the fresh and activated catalysts.

In the direction of preventing catalyst deactivation of earlier Pd–Sb/TiO_2 catalysts[8] and to further enhance the selectivity of BA, an attempt has now been made to modify catalyst composition using different promoters like Sn and Bi. Among these promoters, Bi is found to exhibit superior performance. In view of the above, in the first step the Pd–Bi/TiO_2 catalysts with three different Pd : Bi ratios were tested and it was found that the catalyst with Pd : Bi ratio of 0.35 is more effective (X(Tol) = 27%, S(BA) = 95%) compared to the other two catalysts (Fig. 1). The incorporation of Bi has surprisingly enhanced the BA selectivity to $\geqslant$ 95% in addition to preventing the catalyst deactivation. So, it is clear now that the addition of Sb to Pd catalysts (*i.e.* Pd–Sb/TiO_2) results in higher activity but shorter lifetime,[8] on the other hand addition of Bi, though resulting in less activity, improved both the selectivity of BA and the lifetime of the catalysts. Therefore, it was thought that combining these two effects (*i.e.* addition of Bi and Sb to Pd catalysts) might be very useful. In view of this, in the next step, Pd–Sb–Bi/TiO_2 catalysts were prepared and tested, the results of which are also discussed below.

It is evident from Fig. 2 that an increase in Pd loading has an accelerating effect on the activity of the Pd–Sb–Bi/TiO_2 catalysts. The conversion of toluene is increased dramatically from 10 to 71% with an increase in Pd loading from 0.5 to 20 wt%, while it has no significant effect on the selectivity of BA, which remained more or less constant at around 95%. The yield of BA has remarkably increased from 9.8 to 67.5% with an increase in Pd loading.

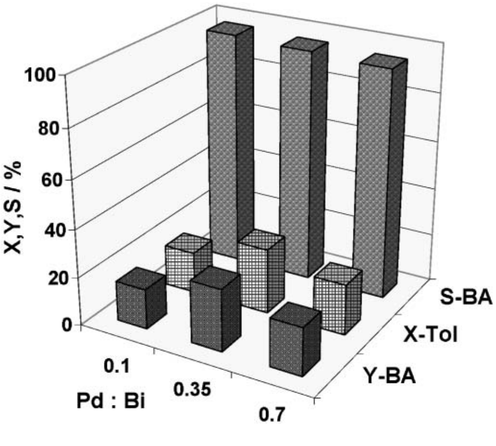

Fig. 1 Influence of Pd : Bi ratio on catalytic performance of Pd–Bi/TiO_2 catalysts.

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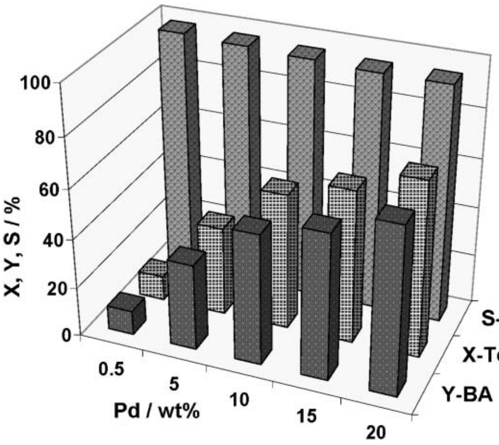

Fig. 2 Influence of Pd loading on acetoxylation activity of Pd–Sb–Bi/TiO_2 catalysts.

Benzaldehyde is the major by-product and the balance is total oxidation products (CO_x).

After detailed analysis of the influence of Pd loading on the acetoxylation activity, the 20% Pd–8% Sb–7% Bi/TiO_2 catalyst is found to exhibit better performance compared to all other catalysts. Therefore, the long term stability of this catalyst was further investigated with time-on-stream for a period of 100 h. It is obvious from Fig. 3 that the catalyst is observed to show low initial activity, which is found to increase progressively up to 50 h, displays maximum conversion ($>$ 70%) and then exhibits quite consistent performance throughout. However, this phenomenon has no effect on the selectivity of BA, which remained more or less constant (95%) right from the beginning. A similar tendency is also observed in all other catalysts irrespective of Pd loading.

However, the origin of the promoting role of Bi on the catalyst life and BA selectivity is still a matter for discussion. Literature reports indicate that the addition of Bi has an influence on the geometric blocking effect of active sites centered on the noble metal, *e.g.*[11] and also the formation of new active centers,[12] which might be responsible for the prevention of present catalyst deactivation and enhanced selectivity of the desired product. One interesting observation on the addition of Bi is the formation of smaller Pd particles (Fig. 4) and decreased surface areas and pore volumes compared to earlier Pd–Sb/TiO_2 catalysts[8] for similar Pd loadings. The Pd–Sb–Bi/TiO_2 catalysts displayed lower activity and higher selectivity compared to Pd–Sb/TiO_2 catalysts.

The results showed that the presence of Sb seems to be essential for obtaining higher activity due to synergetic effects between Sb and Pd[8] and at the same time, the presence of Bi is equally essential for getting high BA selectivity and improved long-term stability.

It was clearly observed that the reaction conditions have brought about drastic changes in the catalyst structure, especially the Pd particle size between fresh and used catalysts. In order to identify the morphological changes during the course of reaction and to check possible reasons for the prevention of deactivation by Bi modification, the 10% Pd–8% Sb–7% Bi/TiO_2 solid was taken as a model catalyst and analysed by TEM at different stages of reaction (*i.e.* after 1 day, 2 days and 4 days tests). The catalyst used for 1 day exhibited both smaller and bigger Pd particles in the range from $<$ 5 to 45 nm. The interesting observation is that the Bi particles, which are located at a considerable distance from the TiO_2 support in the fresh catalyst, are now moved close to the support particles after 1 day tests. After testing for 2 days, the catalyst exhibited bigger Pd particles up to 70 nm in addition to some smaller Pd particles ($\sim$5 nm). In the case of the catalyst used for 4 days, the smaller Pd particles almost disappeared and bigger ones up to 100 nm were formed. The size of the Pd particles around 100 nm is also seen in the used 20% Pd catalyst (Fig. 4). These observations indicate that the size of Pd particles is increasing with time-on-stream, and bigger particles seem to be favourable for better performance.[8]

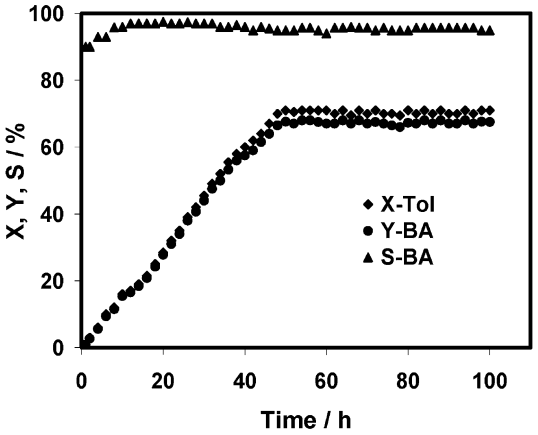

Fig. 3 Catalytic performance of 20% Pd–Sb–Bi/TiO_2 catalyst with time-on-stream.

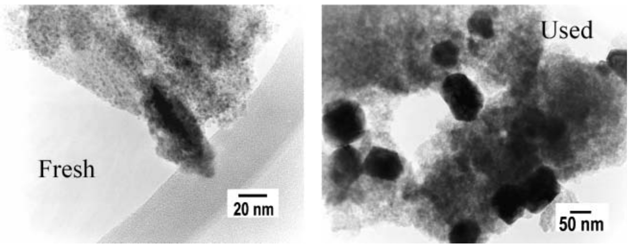

Fig. 4 TEM images of 20% Pd–Sb–Bi/TiO_2 fresh and used catalysts.

In summary, this is a first report mainly on two aspects, i) successful prevention of catalyst deactivation and ii) achieving remarkably high BA selectivity ($\geqslant$ 95%) at high conversion ($>$ 70%) by suitable modification of catalyst composition. Furthermore, novel Pd–Sb–Bi/TiO_2 catalysts have been tested for the first time for the gas phase acetoxylation of toluene. It is proved through the present study that higher Pd loadings are favourable for better performance of catalysts.

Notes and references

1 J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1968, 1331.
2 E. Benazzi, C. J. Cameron and H. Mimoun, *J. Catal.*, 1993, **140**, 311.
3 S. K. Tanielyan and R. Augustine, *J. Mol. Catal.*, 1994, **87**, 311.
4 *US Pat.*, 4 033 999, 1977.
5 *Ger. Pat.,* DE 2 107 913, 1971.
6 L. Eberson and L. Jönsson, *Acta Chem. Scand., Ser. B*, 1974, **28**, 597.
7 T. Komatsu, K. Inaba, T. Uezno, A. Onda and T. Yashima, *Appl. Catal. A.*, 2003, **251**, 315.
8 A. Benhmid, K. V. Narayana, A. Martin and B. Lücke, *Chem. Commun.*, 2004, 2118–2119.
9 T. Miyake, A. Hattori, M. Hanaya, S. Tokumara, H. Hamaji and T. Okada, *Top. Catal.*, 2000, **13**, 243.
10 Patent application submitted to German patent office, (*No: P241303DE-WT*), 2004.
11 T. Mallat, Z. Bodnar, P. Hug and A. Baiker, *J. Catal.*, 1995, **153**, 131.
12 T. Mallat, Z. Bodnar, C. Brönnimann and A. Baiker, *Stud. Surf. Sci. Catal.*, 1994, **88**, 385.