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ChemComm
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One-step synthesis of benzyl acetate by gas phase acetoxylation of toluene over highly active and selective Pd–Sb–TiO$_2$ catalysts†

A. Benhmid, K. V. Narayana, A. Martin* and B. Lücke

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

Received (in Cambridge, UK) 28th April 2004, Accepted 24th June 2004
First published as an Advance Article on the web 2nd August 2004

Significantly high benzyl acetate selectivity of 85% at a toluene conversion of *ca.* 93% was achieved for the first time in a single step by gas phase acetoxylation over highly active and selective Pd–Sb–TiO$_2$ catalysts.

Acetoxylation is an industrially important reaction for producing benzyl esters from alkyl benzenes using carboxylic acids in an oxidising atmosphere. No suitable vapour phase method is available to date for the direct conversion of alkyl benzenes in general and toluene to benzyl acetate in particular. Benzyl acetate (BA) is used chiefly in perfumery, food and also in the chemical industry (notably as a solvent for cellulose acetate). The majority of the work reported so far on the acetoxylation of methyl aromatics (*e.g.* toluene to BA) was carried out under liquid phase conditions and in batch reactors, *e.g.*[1–4] Attempts have also been made over the past few decades to develop suitable vapour phase processes for the direct acetoxylation of toluene.[5,6] Eberson *et al.*[7] achieved only very low yields of acetoxylated products (∼ 1% per pass) even with the addition of various promoters (*e.g.* Au, Bi, Ag–Bi, Au–Bi *etc.*) to Pd catalysts. Very recently, Komatsu *et al.*[8] reported on the gas phase acetoxylation of toluene over SiO$_2$ supported different intermetallic Pd compounds like Pd$_2$Ge, Pd$_5$Ga$_2$, Pd$_3$Pb, Pd$_3$Bi *etc.*; a maximum yield of BA of only around 7% could be achieved.

In this communication, we disclose a first report on vapour phase synthesis of BA in significantly higher yields and explore the influence of Pd loading as well as time-on-stream of the best Pd–Sb–TiO$_2$ catalyst.

Two types of TiO$_2$ (anatase) supported catalysts (mono- and bimetallic) were prepared by impregnation. Pd or Sb anatase supported catalysts were prepared using PdCl$_2$ or SbCl$_3$. The bimetallic catalysts were synthesised in a first step by impregnation of SbCl$_3$ onto the anatase carrier, followed by oven drying and calcination at 400 °C for 3 h. The second step involves the impregnation of PdCl$_2$ to the above solid in a desired amount followed by drying of the resulting solid mass in an oven at 120 °C for 16 h as described elsewhere.[9] The loading of Pd varied in the range from 0.5 to 20 wt% with constant Sb loading (8 wt%).

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 at 2 bars in presence of air. 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 mole ratio of 1 : 4 was pumped to the reactor using an HPLC pump. The product stream was analysed by on line-GC.

Surface areas and pore volumes were drastically decreased from 161 to 42 m^2 g^{-1} and 0.215 to 0.055 cm^3 g^{-1} with an increase in Pd loading from 0.5 to 20 wt%. The XRD reflections correspond to metallic Pd and PdO phases that could be seen in the (fresh) catalysts only with higher Pd loadings of 10 wt% and above. TEM analysis of fresh catalysts showed an increase in the Pd particle size from < 5 nm to about 20 nm with increasing Pd loading.

Our preliminary catalytic tests show poor results on monometallics while the combination of Pd and Sb proved to have an amazing effect on their catalytic properties. Pd alone supported on TiO$_2$ (*i.e.* 5% Pd/TiO$_2$ catalyst) displayed very much less activity ($X_{\text{toluene}} = 2.4\%$; $Y_{\text{BA}} = 2.2\%$) and at the same time Sb alone supported on TiO$_2$ (*i.e.* 8% Sb/TiO$_2$ catalyst) was also found to exhibit poor performance ($X_{\text{toluene}} = 2\%$; $Y_{\text{BA}} = 1.7\%$). However, the combination of both Pd and Sb in appropriate amounts significantly enhanced the activity of the present Pd and Sb catalysts. The activity of 5% Pd–8% Sb–TiO$_2$ catalyst was nearly 16–18 times higher ($X_{\text{toluene}} = 37\%$; $Y_{\text{BA}} = 32\%$) than that of TiO$_2$ supported monometallic either on Pd or Sb catalysts. This observation clearly indicated the existence of significant synergy between Pd and Sb of the present catalysts (Fig. 1).

It is obvious from Fig. 2 that an increase in Pd content has a highly pronounced promotional effect on the catalytic performance of the catalysts. The conversion of toluene has been observed to increase continuously from 16% to 92.6% with increase in Pd loading from 0.5 to 20 wt%, while it has no considerable effect on BA selectivity, which remained more or less constant at around 85%. Benzaldehyde is found to be the major by-product and the balance is total oxidation products (CO$_x$). It was also proved in separate experiments that CO$_x$ is formed mainly by the oxidative decomposition of acetic acid but not from toluene as the reaction temperature is very low. It is also known that the decomposition of acetic acid is relatively much easier compared to toluene. The moles of toluene converted per gram catalyst per hour vary in the range from 9.6 × 10^{-4} to 5.5 × 10^{-3} moles g^{-1} h^{-1}.

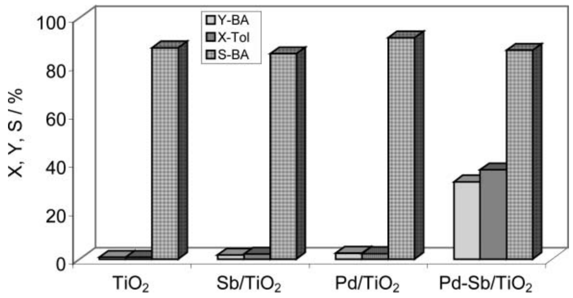

Fig. 1 Synergetic effect between Pd and Sb in Pd–Sb–TiO$_2$ catalysts.

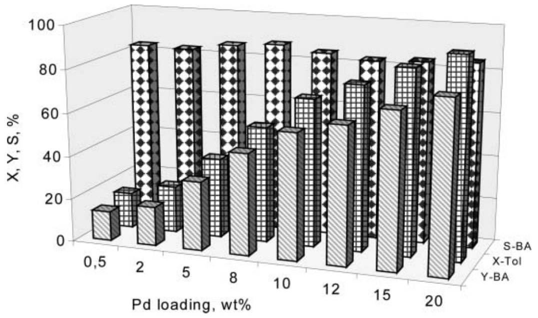

Fig. 2 Influence of Pd loading on the activity and selectivity of Pd–Sb–TiO$_2$ catalysts (p = 2 bar, T = 210 °C, (mole ratios) toluene : acetic acid : O$_2$: inert gas = 1 : 4 : 3: 16, GHSV = 2688 h^{-1} (STP), residence time = 1.34 s).

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† Electronic supplementary information (ESI) available: supporting evidence. See http://www.rsc.org/suppdata/cc/b4/b406396a/

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

DOI: 10.1039/b406396a

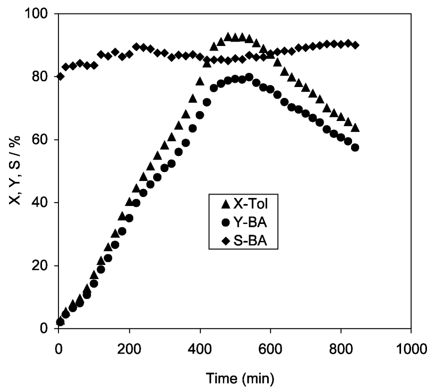

Fig. 3 Catalytic performance of 20% Pd–8% Sb/TiO_2 catalyst with time-on-stream.

The used catalysts exhibited considerably bigger Pd particles up to 100 nm with irregular shapes compared to the fresh catalysts due to agglomeration of Pd during the course of reaction. The catalytic performance was also observed to change in a similar manner to Pd particle size. This fact suggests that the catalytic performance is strongly dependent on the Pd particle size and the larger particles are favourable for better performance of the catalysts, which is in good agreement with literature reports.[2]

TEM and XRD analyses also proved that the growth of particles (agglomeration) occurs only during the course of reaction but not during the activation step (300 °C/2 h/air).

Fig. 3 clearly demonstrates the changes in catalytic performance of the best catalyst, *i.e.* 20% Pd–8% Sb–TiO_2 (anatase), with time-on-stream. The catalysts display a very low initial activity, which is observed to increase considerably with time. Normally, the catalysts are found to exhibit maximum activity after around 7 hours of operation, which may also be the time needed for Pd particle growth during the course of reaction. This observation again provides evidence that the higher activity is associated with larger Pd particles that are formed during the course of reaction only after a certain period of time. Nevertheless, the major problem with these catalysts is deactivation due to considerable amounts of coke deposits. The amount of coke estimated, for instance, in the used 20% Pd–8% Sb–TiO_2 catalyst was 7.3% after *ca.* 900 min. No significant difference in the size of Pd particles between highly active and deactivated catalysts could be seen from TEM. The only difference between these two samples is the amount of coke deposits. This result indicates that the deactivation is mainly due to coke deposition rather than agglomeration of Pd particles, which in fact seemed to be favourable for better performance. However, the regenerated catalysts (250 °C/2 h/air) were found to display consistent performance for a higher number of cycles due to effective removal of coke from the catalyst surface.

In summary, this is a first report on the direct synthesis of BA from toluene by vapour phase acetoxylation with yields higher than 75%. The increase in catalytic activity with Pd loading might be due to an increase in the size of Pd particles and the deactivation due to coke deposition. Nevertheless, further studies are needed to verify the exact nature of the synergy between Pd and Sb and also to explore the precise role of active sites for preventing catalyst deactivation.

Thanks are due to Drs S. Bischoff, M.-M. Pohl and M. Schneider for their help and useful discussions.

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. Tanielyan and R. Augustine, *J. Mol. Catal.*, 1994, **87**, 311.
4 K. Ebitani, K.-M. Choi, T. Mizugaki and K. Kaneda, *Langmuir*, 2002, **18**, 1849.
5 *US pat.*, 4 033 999, 1977.
6 *Ger. pat.*, DE 2 107 913, 1971.
7 L. Eberson and L. Jönsson, *Acta Chem. Scand., Ser. B*, 1974, **28**, 597.
8 T. Komatsu, K. Inaba, T. Uezno, A. Onda and T. Yashima, *Appl. Catal., A*, 2003, **251**, 315.
9 Patent application submitted to German Patent Office, (*No: P241303DE-WT*), 2004.