

## **Novel Pd catalysts with improved performance for vapour phase acetoxylation of toluene**

A. Benhmid, B. Lücke, V. Narayana Kalevaru, A. Martin, U. Dingerdissen

*Institut für Angewandte Chemie Berlin-Adlershof e.V.<sup>‡</sup>, Richard-Willstätter-Str. 12  
D-12489 Berlin, Germany*

Vapour phase acetoxylation of toluene, which is still under developmental stage, is an interesting research field from both academic and industrial viewpoints. The desired product, benzyl acetate (BA) is widely used in perfumery, food and chemical industries. It is known from the state of the art that no apparent success has been achieved to date in terms of achieving higher yields of benzyl acetate with longer life of the catalysts particularly under gas phase conditions. Most of the studies reported so far on BA synthesis via acetoxylation are confined to batch reactors in liquid phase. Against this background, the present study is taken up to develop highly active and selective Pd based catalysts for gas phase acetoxylation of toluene and to carry out a systematic investigation of influence of Pd loading on catalytic performance.

Pd-Sb-TiO<sub>2</sub> catalysts are prepared by impregnating SbCl<sub>3</sub> on anatase, followed by drying and calcination. Afterwards, PdCl<sub>2</sub> was impregnated to the above solid in desired amounts followed by drying [1]. The content of Pd is varied from 0.5 to 20wt%, while the Sb loading kept constant at 8wt%. The catalysts are characterised by N<sub>2</sub>-adsorption, XRD, XPS and TEM. Acetoxylation runs were carried out in a fixed bed stainless steel reactor at 210 °C and 2 bars. Product stream was analysed by on line-GC.

BET surface areas of the catalysts are observed to decrease from 161 to 42 m<sup>2</sup>/g with increase in Pd loading from 0.5 to 20wt%. XRD revealed the presence of Pd and PdO phases in the catalysts with higher Pd loadings of 10wt% and above. TEM showed a significant growth of Pd particles in the used catalysts compared to their fresh ones. Pd loading is found to have an accelerating effect on the activity of the catalysts. The conversion of toluene increased remarkably from 16 to > 90% with increase in Pd loading from 0.5 to 20wt%, while the selectivity of BA remained more or less constant (85%) all the time irrespective of toluene conversion. These Pd-Sb-TiO<sub>2</sub> catalysts were found to deactivate after several hours of operation due to coke deposits, which in turn resulted in loss of both Pd and Sb at the surface as evidenced by XPS. However, they can easily be regenerated in air and reused with consistent performance for more number of cycles. In an attempt to overcome such deactivation problem, we have introduced for the first time, a highly selective and effective gas phase process using Pd-Sb-Bi-TiO<sub>2</sub> catalysts [2]. Using this novel catalyst composition, the major problem of catalyst deactivation could successfully be solved and additionally extremely high selectivity of BA (95%) at a toluene conversion of ≥ 70% has been achieved.

[1] A. Benhmid, K. V. Narayana, A. Martin, B. Lücke, Chem. Commun, 2004, 2118.

[2] A. Benhmid, K. V. Narayana, A. Martin, B. Lücke, M.-M. Pohl, Chem. Commun, 2004, 2416.

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