

Highly Active and Selective Pd–Cu–TiO₂ Catalyst for the Direct Synthesis of Benzyl Acetate by Gas Phase Acetoxylation of Toluene

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Extremely high benzyl acetate selectivity (ca. 94%) at a toluene conversion of ca. 60% was achieved over Pd–Cu–TiO₂ catalyst for the first time by gas phase acetoxylation of toluene with good long-term stability.

The direct oxidation of methyl aromatics to their corresponding aldehydes/alcohols is often unselective as these products undergo further oxidation. This problem can be overcome using suitable catalysts and appropriate auxiliary reagents to produce stable products. Vapor phase acetoxylation is one such example for producing stable end products, particularly to produce various industrially important esters. No suitable method is available till date for the direct conversion of alkyl benzenes in general and toluene to benzyl acetate (BA) in particular, in a single step by vapor phase acetoxylation. BA is used mainly in the perfumery, food, and chemical industry. The most 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.^{1–6} Literature survey reveals that Pd based catalysts are being widely used for toluene acetoxylation both in liquid and vapor phase. However, no apparent success is achieved in terms of obtaining higher yields of BA. Furthermore, all these processes/catalysts reported so far suffer from various drawbacks like easy deactivation, leaching problems etc. An attempt by Eberson and Jönsson⁷ achieved only very low yields of acetoxylation products ($\approx 1\%$ per pass). Very recent report by Komatsu et al.⁸ on the gas phase acetoxylation of toluene over SiO₂ supported different intermetallic Pd compounds like Pd₂Ge, Pd₅Ga₂, etc., a maximum yield of BA of around 7% could only be achieved.

In this communication, we explore the influence of various promoters on the catalytic performance of Pd acetoxylation catalysts and report for the first time Pd–Cu–TiO₂ as highly efficient catalyst system.

The preparation of catalyst involves mainly two steps. The first step deals with the impregnation of the promoter (e.g., Sb, Sn, Bi, Cu) on to the TiO₂ (anatase), followed by oven drying and calcination at 400 °C for 3 h. The second step involves the impregnation of Pd source (PdCl₂) 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 sources of promoters are SbCl₃, SnCl₂·2H₂O, BiCl₃, and CuCl₂·2H₂O. The content of Pd is kept constant at 10 wt % in every case, while the contents of all these promoters are selected to be 8 wt % except Bi (7 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. 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 a HPLC pump.

The product stream was analyzed on line by GC.

The BET surface areas and pore volumes of the fresh catalysts are varied in the range from 44 to 78 m²/g and 0.109 to 0.127 cm³/g depending upon the nature of promoter used. TEM analysis of fresh catalysts with different promoters showed that the size of Pd particles is found to be dependent on the type of promoter used. Bigger Pd particles exhibited by Sb (ca. 10 nm) and smaller by Bi (≈ 1 nm). The size of Pd particles displayed by different promoters are in the following order: Sb > Sn > Cu > Bi. The morphology of Pd particles is mostly spherical. The fresh Pd–Cu–TiO₂ catalyst showed Pd particles in the range of 1 to 3 nm, with narrow size distribution.

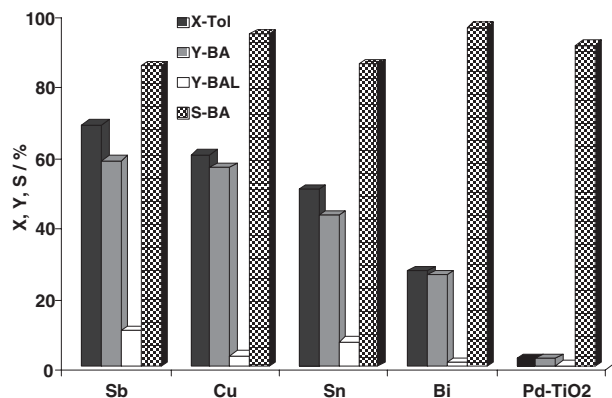


Figure 1. Influence of promoter on catalytic performance of Pd–M–TiO₂ catalysts (M = Sb, Bi, Sn, Cu); X-Tol: toluene conversion, Y-BA: benzyl acetate yield, Y-BAL: benzaldehyde yield, S-BA: benzyl acetate selectivity.

Our preliminary catalytic tests showed poor performance of monometallics (i.e., Pd alone supported on TiO₂)¹⁰ while the combination of Pd with any of the promoter used in the present study proved an amazing effect on their catalytic performance due to synergetic effects between Pd and promoter. The influence of promoter on the catalytic performance is shown in Figure 1, which clearly indicates that the nature of promoter has a strong influence on the activity, selectivity, and the life of the catalyst. Among all the promoters studied, Sb is found to display best performance giving 68% conversion of toluene and 85% selectivity of BA. The order of the reactivity of these promoters is Sb > Cu > Sn > Bi. It is noteworthy that both Sb and Sn promoted catalysts though they exhibit considerably good performance, they were found to deactivate after some hours of catalytic tests owing to coke deposition. However, no such deactivation problem was observed in case of Cu and Bi promoted catalysts, which additionally exhibit extremely high selectivity of BA (ca. 95%) compared to the other two catalysts. Between these two advantageous systems, Cu promoted catalyst

displayed better performance giving higher activity and hence this Pd–Cu–TiO₂ catalyst has become the main focus of the present study. This catalyst gave 60% conversion of toluene and 94% selectivity of BA without any deactivation. The major by-product is benzaldehyde (BAL) and the balance is total oxidation products (CO_x). In addition, the catalytic performance of pure Pd–TiO₂ catalyst without promoter ($X_{\text{Tol}} = 2.4\%$ & $Y_{\text{BA}} = 2.2\%$) is also given for better comparison on the influence of promoter.

Figure 2 demonstrates the time-on-stream behavior of Pd–Cu–TiO₂ catalyst over a period of 160 h. It is evident from the figure that the catalyst is found to exhibit very low initial activity (<5%), which is increased significantly with time-on-stream reaching maximum at 60% after about 60 h and then displayed consistent performance throughout the catalytic runs. It is seen from TEM analysis of used catalysts that the size of Pd particles is significantly growing during the course of reaction and it is also observed in earlier experiments that bigger Pd particles are much favorable for better performance. This might be the reason for attaining steady-state conditions only after a certain period of time, which is the required time for Pd particle growth to an appropriate size.

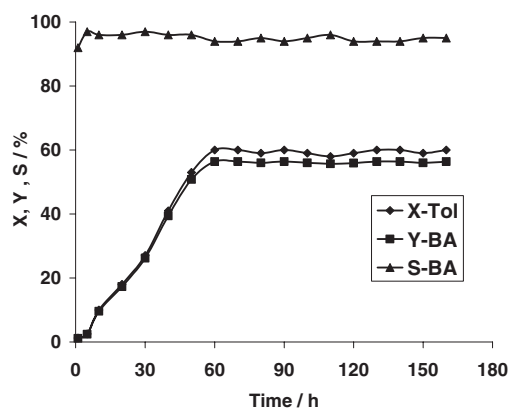


Figure 2. Time-on-stream analysis of 10% Pd–Cu–TiO₂ catalyst (denotation as for Figure 1).

Used Pd–Cu–TiO₂ catalyst exhibited significantly bigger Pd particles even up to 150 nm indicating particle growth during the course of reaction due to agglomeration (Figure 3). Similar such growth of Pd particles is also observed in case of the catalysts with other promoters such as Sb, Sn, Bi. Based on all these observations it seems more probable that higher catalyst activity is

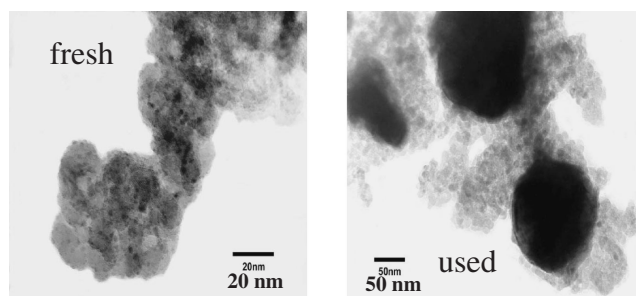


Figure 3. TEM images of the fresh and used Pd–Cu–TiO₂ catalysts.

associated with bigger Pd particles, which is in good agreement with earlier investigations.¹⁰

In summary, this is a first report on the direct synthesis of BA with higher yield (ca. 55%) and extremely high selectivity of BA (94%) by gas phase acetoxylation. Furthermore, incorporation of Cu and Bi has successfully solved the problem of the catalyst deactivation, while Cu is found to be more effective than Bi. However, additional experiments are necessary for better understanding of the nature of the active sites and the precise role of the Cu that prevents catalyst deactivation.

References and Notes

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