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Oxidation of Toluene to Benzoic Acid Catalyzed by Platinum Supported on Zirconia in the Liquid Phase-Solvent Free Conditions

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Abstract Toluene oxidation over platinum supported on zirconia under solvent free conditions in a batch reactor was studied in the temperature range 60–90 °C. Molecular oxygen was used as oxidant. The catalyst was highly active and selective for benzoic acid formation. Some conversion to benzyl benzoate, *trans*-stilbene and methyl biphenyl carboxylic acid was also observed when the reaction was studied for >3 h. The reaction is taking place at considerably lower temperature than the reported solvent free oxidation reactions of toluene.

Keywords Selective oxidation · Toluene · Benzoic acid · *trans*-Stilbene · Methyl biphenyl carboxylic acid · Platinized zirconia

1 Introduction

Selective catalytic oxidation of toluene to corresponding alcohol, aldehyde and carboxylic acid by molecular oxygen is of great economical and industrial importance. Industrially, the oxidation of toluene to benzoic acid (BzOOH) with molecular oxygen is a key step for phenol synthesis in the Dow Phenol process and for ε-caprolactum formation in Snia-Viscosia process [1–7]. Toluene is also a representative of aromatic hydrocarbons categorized as hazardous material [8]. Thus development of methods for the oxidation of aromatics such as toluene is also important for environmental reasons. The commercial production of benzoic acid via the catalytic oxidation of toluene is achieved by heating a solution of the substrate, cobalt acetate and bromide promoter in acetic acid to 250 °C, with molecular oxygen, at high pressure. Although complete conversion is achieved, however, the use of acidic solvents and bromide promoter results in difficult separation of products and catalyst, large volume of toxic waste and equipment corrosion. The system requires very expensive, specialized equipments, fitted with extensive safety features. Operating under such extreme conditions consumes large amount of energy. Therefore, attempts are being made to make this oxidation more environmentally benign by performing the reaction in the vapor phase using a variety of solid catalysts [9, 10]. However, liquid-phase oxidation is easy to operate and achieve high selectivity under relatively mild reaction conditions. Many efforts have been made to improve the efficiency of toluene oxidation in the liquid phase, however, most investigation still focus on homogeneous systems using volatile organic solvents. Employing heterogeneous catalysts in liquid-phase oxidation of toluene without solvent would make the process more environmentally friendly. Bastock et al. have reported [11] the oxidation of toluene to benzoic acid in solvent free conditions using a commercial heterogeneous catalyst Envirocat EPAC in the presence of catalytic amount of carboxylic acid as promoter at atmospheric pressure. The reaction was performed at 110–150 °C, with oxygen flow rate of 400 mL/min. The isolated yield of benzoic acid was 85% in 22 h. Subrahmanyan et al. [12] have performed toluene oxidation in solvent free conditions using vanadium substituted aluminophosphate or aluminosilicates as catalyst. Benzaldehyde (BzH) and benzoic acid were the main products when *tert*-butyl hydro peroxide was used as the oxidizing agent while cresols were formed when H_2O_2 was used as oxidizing agent.

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Raja et al. [13, 14] have also reported the solvent free oxidation of toluene using zeolite encapsulated metal complexes as catalysts. Air was used as oxidant (3.5 MPa). The highest conversion (45.1%) was achieved with manganese substituted aluminum phosphate with high benzoic acid selectivity (83.4%) at 150 °C in 16 h. Li et al. [15, 16] have also reported manganese oxide and copper manganese oxide to be active catalysts for toluene oxidation to benzoic acid in solvent free conditions with molecular oxygen (1.0 MPa) at 190–195 °C. Recently it was observed in this laboratory [17] that when toluene was used as a solvent for benzyl alcohol (BzOH) oxidation by molecular oxygen at 90 °C in the presence of Pt/ZrO_2 as catalyst, benzoic acid was obtained with 100% selectivity. The mass balance of the reaction showed that some of the benzoic acid was obtained from toluene oxidation. This observation is the basis of the present study for investigation of the solvent free oxidation of toluene using Pt/ZrO_2 as catalyst.

2 Experimental

2.1 Material

$ZrOCl_2 \cdot 8H_2O$ (Merck, 8917), NH_4OH (BDH, 27140), $AgNO_3$ (Merck, 1512), $PtCl_4$ (Acros, 19540), benzyl alcohol (Merck, 9626), benzaldehyde (Scharlu, BE0160), toluene (BDH, 10284), phenol (Acros, 41717), benzoic acid (Merck, 100136) and *trans*-stilbene (Aldrich, 13,993-9) were used as received.

H_2 (99.999%) was prepared using hydrogen generator (GCD-300, BAIF). Nitrogen and Oxygen were supplied by BOC Pakistan Ltd. and were further purified by passing through traps (C.R.S.Inc.202268) to remove traces of water and oil. Traces of oxygen from nitrogen gas were removed by using specific oxygen traps (C.R.S.Inc.202223).

2.2 Catalyst Preparation and Characterization

Monoclinic zirconia was used as a support for platinum. It has been shown earlier that monoclinic zirconia was a more effective catalyst than tetragonal zirconia for alcohol oxidation in solvent free conditions [18, 19].

Zirconia [17–20] was prepared using an aqueous solution of zirconyl chloride with the drop wise addition of NH_4OH for 4 h (pH 10) with continuous stirring. The precipitate was washed with triply distilled water using a Soxhlet's apparatus for 24 h. The Cl^{-1} test with $AgNO_3$ was found to be negative. Precipitate was dried at 110 °C for 24 h. After drying it was calcined with programmable heating at a rate of 0.5 °C/min to reach 950 °C and was kept at the same temperature for 4 h. Nabertherm C-19 programmed control furnace was used for calcinations. Supported Catalysts were prepared by incipient wetness technique. For this purpose calculated amount (wt%) of the precursor compound ($PtCl_4$) was taken in a crucible and triply distilled water was added to make a paste. Then the required amount of the support (ZrO_2) was mixed with it to make a paste. The paste was thoroughly mixed and dried in an oven at 110 °C for 24 h and then grounded. The catalyst was sieved and 80–100 mesh portions were used for further treatment. The grounded catalyst was calcined again at the rate of 0.5 °C/min to reach 750 °C or 950 °C and was kept at the same temperature for 4 h, after which it was reduced in H_2 flow at 280 °C for 4 h.

BET surface area of the catalyst was determined using a Quanta chrome (Nova 2200e) surface area and pore size analyzer. Samples were degassed at 110 °C for 2 h prior to determination. XRD analyses were performed on a JEOL (JDX-3532) X-ray diffractometer using CuKα radiation with a tube voltage of 40 kV and 20 mA current. SEM was recorded on a JEOL-l 50 H Super Probe 733.

2.3 Reaction Procedure

All the experiments were carried out in a magnetically stirred Pyrex glass three-necked batch reactor (Height 19 cm, ID 3 cm) provided with reflux condenser and a mercury thermometer, for measuring the reaction temperature. Reaction temperature was maintained by using heating tapes. A predetermined quantity of Toluene (10 mL) was taken in the reactor, Pt/ZrO_2 (0.2 g) was added and O_2 (at atmospheric pressure) was passed through the reaction mixture (usually at 40 mL min^{-1}), at a fixed temperature, (60–90 °C). Samples were withdrawn from the reaction mixture at predetermined time intervals. The reaction mixture was filtered to remove the catalyst and analyzed. The changes in the concentration of toluene and its products benzyl alcohol, benzaldehyde, benzoic acid, benzyl benzoate, *trans*-stilbene and methyl biphenyl carboxylic acid were monitored by UV–VIS spectroscopy, gas chromatography and thin layer chromatography [15, 16, 21, 22]. Thin layer chromatographic analysis was carried out using standard chromatographic plates (Merck) with silica gel 60 F_{254} support (Merck, TLC: 105,554 and PLC: 113,793). Ethyl acetate (10%) in cyclohexane was used as eluent. Identification of products was made by comparison of the UV–Visible and FTIR spectra of the products with that of the standards. Shimadzu UV-160A was used for UV–Visible Spectra. Diffuse reflectance spectra of solids (*trans*-Stilbene) were recorded on Shimadzu, IRPrestigue-21, FTIR-8400S, using diffuse reflectance accessory [DRS-8000A]. Solid samples were diluted with KBr before measurement. The spectra were recorded with resolution of 4 cm^{-1} with 50 accumulations.

3 Results and Discussion

3.1 Catalyst Characterization

BET surface area was 65 and 183 $m^2\ g^{-1}$ for ZrO_2 and Pt/ZrO_2, respectively. Figure 1 shows SEM images which reveal that the Pt/ZrO_2 has smaller particle size than that of ZrO_2 which may be due to further temperature treatment or reduction process. The high surface area of Pt/ZrO_2 in comparison to ZrO_2 could be due to its smaller particle size.

Figure 2a, b shows the diffraction pattern for uncalcined ZrO_2 and ZrO_2 calcined at 950 °C. Diffraction pattern for ZrO_2 calcined at 950 °C was dominated by monoclinic phase (major peaks appears at $2\theta = 28.18°$ and 31.38°) [23–25]. Figure 2c, d shows XRD patterns for a Pt/ZrO_2 calcined at 750 °C both before and after reduction in H_2. The figure revealed that Pt/ZrO_2 calcined at 750 °C exhibited both the tetragonal phase (major peak appears at $2\theta = 30.94°$) and monoclinic phase (major peaks appears $2\theta = 28.18°$ and 31.38°). The reflection was observed for Pt at $2\theta = 39.79°$ which was not fully resolved due to small content of Pt ($\sim$1 wt%) as also concluded by Perez-Hernandez et al. [26].The reduction processing of Pt/ZrO_2 affects crystallization and phase transition, resulting in certain fraction of tetragonal ZrO_2 transferred to monoclinic ZrO_2 as also reported else where [27]. However, the XRD pattern of Pt/ZrO_2 calcined at 950 °C (Fig 2e, f) did not show any change before and after reduction in H_2 and were fully dominated by monoclinic phase. However, a fraction of tetragonal zirconia was present as reported by Liu et al. [20].

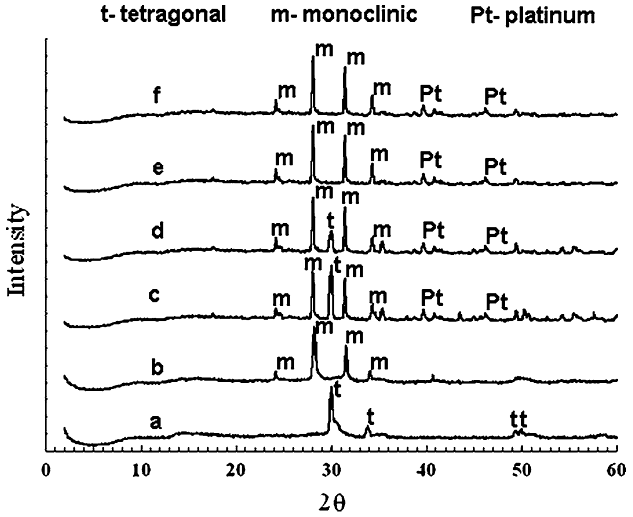

Fig. 2 XRD pattern of ZrO_2 and Pt/ZrO_2. (a) ZrO_2 (uncalcined), (b) ZrO_2 (calcined at 950 °C), (c) Pt/ZrO_2 (unreduced, calcined at 750 °C) and (d) Pt/ZrO_2 (calcined at 750 °C and reduced in H_2). (e) Pt/ZrO_2 (unreduced, calcined at 950 °C) and (f) Pt/ZrO_2 (calcined at 950 °C and reduced in H_2)

3.2 Catalytic Activity

In this work we first studied toluene oxidation at various temperatures (60–90 °C), with oxygen or air passing through the reaction mixture (10 mL of toluene and 200 mg of 1(wt)% Pt/ZrO_2) with continuous stirring (900 rpm). The flow rate of oxygen and air was kept constant at 40 mL/min. Table 1 present these results. The known products of the reaction were benzyl alcohol, benzaldehyde and benzoic acid. The mass balance of the

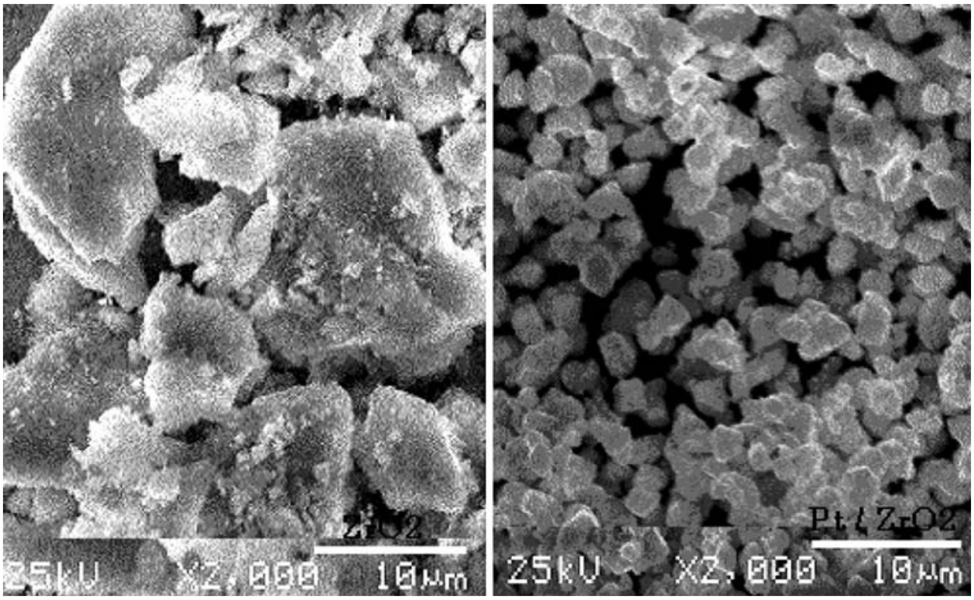

Fig. 1 SEM images of ZrO_2 (calcined at 950 °C) and Pt/ZrO_2 (calcined at 950 °C and reduced in H_2)

Table 1 Oxidation of toluene at various temperatures

T (°C)	Oxidant	Selectivity (%)			Loss[a] (%)	Conversion (%)	TOF[b]
		BzOH	BzH	BzOOH			
60	O_2	45.8	17.7	24.0	1.2	9.6	293
70	O_2	22.1	18.2	53.9	0.9	15.4	470
80	O_2	12.1	21.8	62.3	0.9	23.9	729
90	O_2	6.5	19.6	70.4	1.3	37.2	1135
90	Air	25.0	16.5	51.6	1.3	18.8	574

Reaction conditions: catalyst (0.2 g), toluene (10 mL), pO_2 (101 kPa), flow rate of O_2/Air (40 mL/min)

[a] Toluene lost (mole (%)) not accounted for

[b] TOF (turnover frequency): molar ratio of converted toluene to the platinum content of the catalyst per unit time (h^{-1})

reaction showed some loss of toluene (~1%). Conversion rises with temperature from 9.6% to 37.2%. The selectivity for benzyl alcohol is higher than benzoic acid at 60 °C. At 70 °C and above the reaction is more selective for benzoic acid formation70 °C and above. The reaction is highly selective for benzoic acid formation (>70%) at 90 °C. Reaction can also be performed in air where 18.8% conversion is achieved at 90 °C, with 25% selectivity for benzyl alcohol, 16.5% for benzaldehyde and 51.6% for benzoic acid. Comparison of these results with other solvent free systems shows that Pt/ZrO_2 is very effective catalyst for toluene oxidation. Higher conversions are achieved at considerably lower temperatures and pressure than other solvent free systems [11–16]. The catalyst is used with out any additive or promoter. The commercial catalyst (Envirocat EPAC) requires trimethylacetic acid as promoter with a 1:1 ratio of catalyst and promoter [11]. The turnover frequency (TOF) was calculated as the molar ratio of toluene converted to the platinum content of the catalyst per unit time (h^{-1}). TOF values are very high even at the lowest temperature of 60 °C.

3.2.1 Time Profile Study

The time profile of the reaction is shown in Fig. 3, where a linear increase in conversion is observed with the passage of time. An induction period of 30 min is required for the products to appear. At the lowest conversion (<2%) the reaction is 100% selective for benzyl alcohol (Fig. 4). Benzyl alcohol is the main product until the conversion reaches ~14%. Increase in conversion is accompanied by increase in the selectivity for benzoic acid. Selectivity for benzaldehyde (~20%) is almost unaffected by increase in conversion. This reaction was studied only for 3 h. The reaction mixture becomes saturated with benzoic acid, which sublimes and sticks to the walls of the reactor.

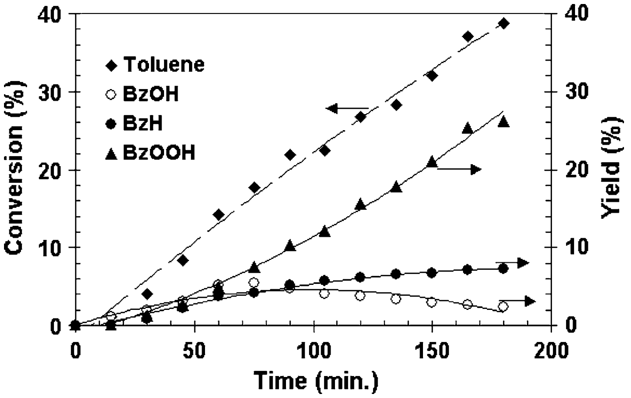

Fig. 3 Time profile for the oxidation of toluene. Reaction conditions: catalyst (0.2 g), toluene (10 mL), pO_2 (101 kPa), flow rate (40 mL/min), temperature (90 °C), stirring (900 rpm)

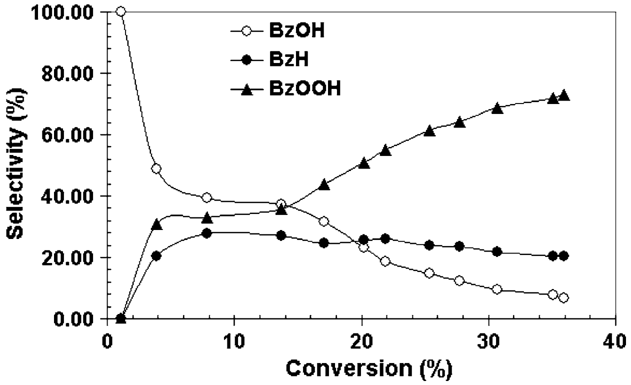

Fig. 4 Selectivity of toluene oxidation at various conversions. Reaction conditions: catalyst (0.2 g), toluene (10 mL), pO_2 (101 kPa), flow rate (40 mL/min), temperature (90 °C), stirring (900 rpm)

3.2.2 Effect of Oxygen Flow Rate

Effect of the flow rate of oxygen on toluene conversion was also studied. Figure 5, shows this effect. It can be seen that with increase in the flow rate both toluene conversion and selectivity for benzoic acid increases. Selectivity for benzyl alcohol and benzaldehyde decreases with increase in the flow rate. At the oxygen flow rate of 70 mL/min the selectivity for benzyl alcohol becomes ~0 and for benzyldehyde ~4%. This shows that the rate of reaction and selectivity depends upon the rate of supply of oxygen to the reaction system.

3.2.3 Appearance of Trans-Stilbene and Methyl biphenyl carboxylic acid

Toluene oxidation was also studied for the longer time of 7 h. In this case 20 mL of toluene and 400 mg of catalyst (1% Pt/ZrO_2) was taken and the reaction was conducted at 90 °C as described earlier. After 7 h the reaction mixture was converted to a solid apparently having no liquid and

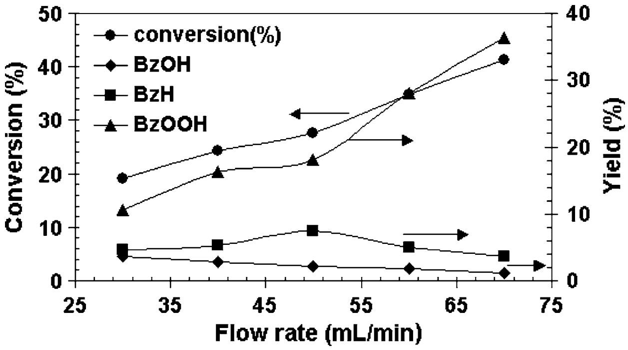

Fig. 5 Effect of flow rate of oxygen on the oxidation of toluene. Reaction conditions: catalyst (0.4 g), toluene (20 mL), pO_2 (101 kPa), temperature (90 °C), stirring (900 rpm), time (3 h)

therefore, the reaction was stopped. The reaction mixture was cooled to room temperature and more toluene was added to dissolve the solid and then filtered to recover the catalyst. Excess toluene was recovered by distillation at lower temperature and pressure until a concentrated suspension was obtained. This was cooled down to room temperature, filtered and washed with a little toluene and sucked dry to recover the solid. The solid thus obtained was 11.2 g. Preparative TLC analysis showed that the solid mixture was composed of five substances. These were identified as benzaldehyde (yield, mol%, 2.2%), benzoic acid (29.6%), benzyl benzoate (3.4%), *trans*-stilbene (5.3%) and 4-methyl-2-biphenylcarboxylic acid (10.8%).The rest (~4%) could be identified as tar due to its black color. Figure 6 shows the conversion of toluene and the yield (mol%) of these products. *Trans*-stilbene and methyl biphenyl carboxylic acid were identified by their melting point and UV–Visible and IR spectra. The Diffuse Reflectance FTIR spectra (DRIFT) of *trans*-stilbene (both of the standard and experimental product) is given in Fig. 7. The oxidative coupling of toluene to produce trans-stilbene has been reported widely [28–32]. Kai et al. [32] have reported the formation of stilbene and bibenzyl from the oxidative coupling of toluene catalyzed by PbO. However, the reaction was conducted at a higher temperature (525–570 °C) in the vapor phase. Daito et al. [33] have patented a process for the recovery of benzyl benzoate by distilling the residue remaining after removal of un-reacted toluene and benzoic acid from a reaction mixture produced by the oxidation of toluene by molecular oxygen in the presence of a metal catalyst. Beside the main product, benzoic acid, they have also given a list of >20 by products. Most of these byproducts are due to the oxidative coupling/oxidative dehydrocoupling of toluene. Methyl biphenyl carboxylic acid (mp 144–146 °C) is one of these by products identified in the present study. Besides these by products they have also recovered the intermediate products in toluene oxidation benzaldehyde and benzyl alcohol and esters formed by esterification of benzyl alcohol with a variety of carboxylic acids inside the reactor. The absence of benzyl alcohol (Figs. 3, 6) could be due to its esterification with benzoic acid to form benzyl benzoate.

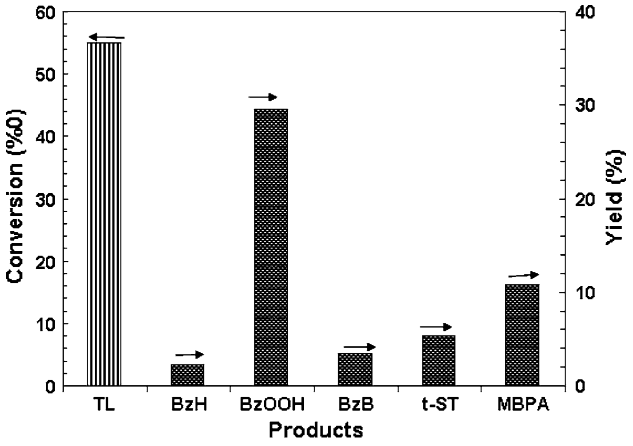

Fig. 6 Conversion of toluene after 7 h of reaction. TL: toluene, BzH: benzaldehyde, BzOOH: benzoic acid, BzB: benzyl benzoate, *t*-ST: *trans*-stilbene, MBPA: methyl biphenyl carboxylic acid reaction. Conditions: toluene (20 mL), catalyst (400 mg), pO_2 (101 kPa), flow rate (40 mL/min), agitation (900 rpm), temperature (90 °C)

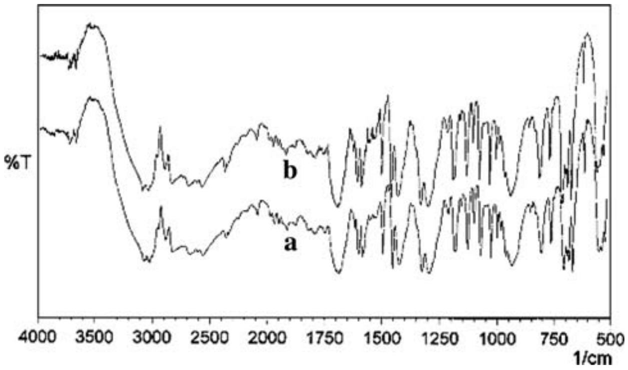

Fig. 7 Diffuse reflectance FTIR (DRIFT) spectra of trans-stilbene, (a) standard and (b) isolated product (mp = 122 °C)

4 Conclusions

Pt/ZrO_2 is an active catalyst for toluene partial oxidation to benzoic acid at 60–90 °C in solvent free conditions. The rate of reaction is limited by the supply of oxygen to the catalyst surface. Selectivity of the products depends upon the reaction time on stream. With a reaction time ≤ 3 h benzyl alcohol, benzaldehyde and benzoic acid are the only products identified. After 3 hours of reaction time benzyl benzoate, *trans*-stilbene and methyl biphenyl carboxylic acid appear along with benzoic acid and benzaldehyde. In both the cases benzoic acid is the main product (selectivity $\geq 60\%$).

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