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Catalytic transfer hydrogenation: *o*-nitro anisole to *o*-anisidine, some process development aspects

P. Haldar, V.V. Mahajani*

Chemical Engineering Division, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400019, India

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Abstract

The catalytic transfer hydrogenation of *o*-nitro anisole to *o*-anisidine was studied in the temperature range 35–85 °C with ammonium formate as H-donor and *iso*-propanol as solvent using Pd/C as catalyst above agitation speed 1000 rpm. The substrate feed concentration was varied in the range from 0.068 to 0.341 kmol/m^3 while catalyst loading was in the range 1.25–10% (w/w) of *o*-nitro anisole. The intermediate, hydroxylamine, was detected. In 130 min, all *o*-nitro anisole was converted with 99% selectivity towards *o*-anisidine. The catalyst has considerable reusability and was regenerated after deactivation without any significance loss in activity. Reliable methods for product separation and treatment of aqueous stream obtained after washing and solvent recovery are proposed. The possibility of Fenton Chemistry to treat aqueous waste stream was explored and found suitable.

Keywords: Transfer hydrogenation; *o*-Nitro anisole; Catalyst (Pd/C); Ammonium formate

1. Introduction

Safety, health and environmental (SHE) management issues are of prime importance in development of reduction as a unit process to manufacture speciality chemicals. Small to medium scale manufacturers might not adequately be equipped to handle reduction reaction by catalytic hydrogenation (using H_2 gas under pressure and have temperature at times exceeding 100 °C) as in the case of large-scale manufacture of bulk chemicals such as aniline from nitrobenzene. In such a situation catalytic transfer of hydrogen, where hydrogen donors are used instead of hydrogen (H_2) gas, plays an important role in the above context, specially, for small to medium scale manufacturers. The safety issues in conventional catalytic hydrogenation mainly due to H_2 and other volatile solvents used can be obviated by using suitable H-donor. Further aqueous solutions of H-donors are used. The presence of water (liquid and vapour) adds to the safety. Of course, safety related issues pertaining to the solvent used (low molecular weight alcohols) still remain there. In catalytic transfer hydrogenation a H-donor is used, which under relatively mild conditions donates hydrogen to an acceptor substrate and consequently gets oxidized. The commonly used H-donors are NH_4, Na or K formate and hydrazine depending upon price and ease of availability and its integration with existing production facility. For example, if organization is having Na-formate as the byproduct from other operation, one would prefer Na-formate as H-donor. The H-donor used for heterogeneous systems often give volatile products (e.g. CO_2, NH_3 from ammonium formate and N_2 from hydrazine) and removal of these volatiles from the reaction mixture precludes a state of equilibrium being reached. By increasing the reaction temperature the shift of equilibrium towards product side simply leads to increase in the rate of reaction. However, the other factor may determine optimal condition because of possibility of over reduction, isomerisation or decomposition of the substrate, which may occur as side reaction at elevated temperature.

A new dimension is opened up because the choice of H-donor can effect the reaction through its competitive adsorption on to the catalytic surface. The catalyst plays a very

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* Corresponding author. Tel.: +91 22 24145616; fax: +91 22 24145614.
E-mail address: vvm@udct.org (V.V. Mahajani).

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important role in transferring hydrogen from the donor to acceptor substrate molecule that is utilized for transfer hydrogenation. Both homogeneous and heterogeneous catalyst systems are reported [1a,1b], with the recovery of catalyst from homogeneous system is often cumbersome. The ease of separation, compromised against the rate of reaction, favors the heterogeneous system. The most popular heterogeneous catalysts are based on transition group metals e.g. Pd, Pt, Ru etc. supported on activated carbon [1a]. The catalytic activity of the above elements and their salts or complexes is the result of a delicate balance of valence state and strength of chemical bonds they form with substrate and solvent molecules [13]. However, some alloys having catalytic activity [2], show the synergistic effect only under physically mixed conditions.

The correct choice of a solvent is a critical factor that governs the catalyst activity in transfer hydrogenation. The coordination of the catalyst in heterogeneous system must be competitive with binding of H-donor to acceptor [3]. The viscosity, thermal stability, ease of availability, toxicity, effluent treatment required and capability of stabilizing the transition state of the reaction are considered important criteria for the screening of solvents.

In this present research investigation, we have undertaken process development studies in the catalytic transfer hydrogenation of *o*-nitro anisole to *o*-anisidine.

The commercial importance of *o*-anisidine is well known in the manufacture of dye intermediates [4] (both azo and aniline), pharmaceutical intermediates [5], etc. There is scanty information available in the published literature on the process engineering aspects of catalytic transfer of hydrogen of *o*-nitro anisole to yield *o*-anisidine. It was, therefore, thought desirable to undertake bench scale investigation of various parameters affecting conversion, selectivity and hence overall yield. The parameters included speed of agitation, reaction temperature, catalytic element loading, type of H-donor, its relative amount, solvents used and reactant concentration. The study is expected to aid process development.

2. Experimental

The details of the experimental set-up, experimental procedures and analytical techniques are presented in this section.

2.1. Materials

The raw material and the product *o*-nitro anisole (ONA) and *o*-anisidine (OA), respectively, were gift samples from the local industry. Ammonium formate used as H-donor was obtained from M/s S.D. Fine Chemicals (India) Ltd. The solvents, methanol (CH_3OH), ethanol (C_2H_5OH) and *iso*-propanol (C_3H_7OH) were used as such technical grade without purifying and were obtained from E. Merck (India) Ltd. The reagents used for analysis on high performance thin layer chromatography (HPTLC) were methanol (HPLC grade) as a diluent of product mixture and xylene (AR grade) for developer (obtained from M/s S.D. Fine Chemicals (India) Ltd.).

2.2. Experimental set-up

The catalytic transfer hydrogenation of *o*-nitro anisole to *o*-anisidine was studied in a mechanically agitated glass reactor, a capacity of 500 cm^3 and having 7.5 cm i.d., simulating an industrial contactor. The glass reactor was equipped with four-blade plate type impeller, diameter 2.5 cm, baffles and a thermo-well for measuring reaction mixture temperature. A reflux condenser with provision for chilled water as a coolant was also mounted on the reactor to condense and reflux solvent vapors. The entire set-up was immersed in a constant temperature water bath, maintained by using temperature indicator and controller (TIC) within ±1 °C of the set temperature. The schematic diagram of the experimental set-up is exhibited in Fig. 1.

2.3. Catalyst preparation

For preparation of the catalyst known amount of $PdCl_2$ was dissolved in HCl and added to a suspension of previously washed (with 10% HNO_3 and methanol) activated carbon. Catalyst of desired strength was prepared by reduction with formaldehyde under alkaline condition at 80 °C [6]. The catalyst was washed free of chloride (Cl^-) ions till the filtrate tested by silver nitrate ($AgNO_3$), indicated absence of chloride. After air-drying the filter cake was effectively dried in a desiccator over $CaCl_2$. The dried catalyst has mean particle size 27.53 μm (analyzed by Coulter LS 230).

2.4. Experimental procedure

A measured amount of reactant, *o*-nitro anisole, organic solvent (e.g., methanol, ethanol or *iso*-propanol) and prede-

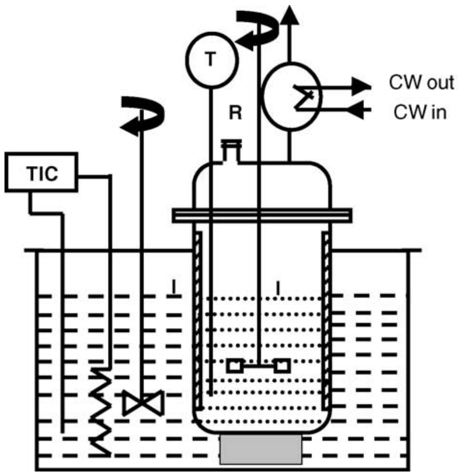


Fig. 1. Experimental set-up for catalytic transfer hydrogenation. CW, cooling water; H, heater; R, inlet; I, impeller; TIC, temperature indicator and controller; T, thermometer.

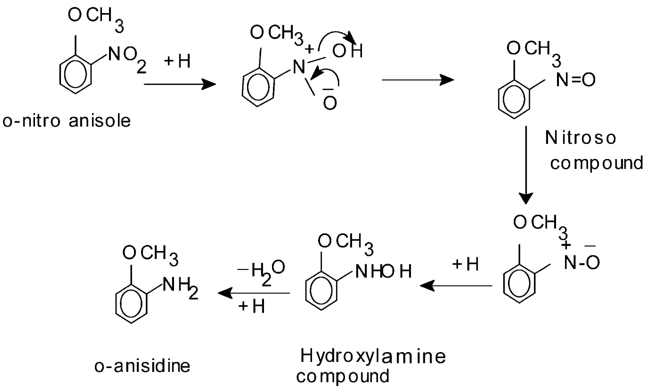
termined volume of aqueous solution of weighted H-donor (e.g., ammonium formate and sodium formate) were taken in a glass reactor. When the temperature of the reaction mixture reached the desired value, the suspension of catalyst in the same organic solvent, that had been pre-heated to temperature close to reaction mixture, was added. This was considered as time zero. The total volume of liquid in reactor was approximately 120 cm^3. The samples were taken out at various time intervals. The reaction was stopped by removing the catalyst from sample mixture (filtration was very fast) and then cooling to 5 °C. These samples were diluted with methanol (HPLC grade) and were used for analytical purpose.

2.5. Analytical technique

The samples were analyzed using high performance thin layer chromatography (HPTLC), using an applicator and a densitometer (Desaga, Germany). A UV-detector was used for scanning. The HPTLC plates used were locally purchased from M/s E. Merk (India) Ltd. The developer used was A.R. grade xylene. The precalibration was done for sample analysis. In order to detect hydroxylamine, which is one of the intermediates, in a sample having 50–60% conversion, a 3 M HCl solution was added to chill the sample for about 1 h. The mass was extracted and analyzed. The infrared spectroscopy (FTIR, Perkin Elmer Ltd., UK) of the sample was performed to detect the functional groups of the products formed.

3. Results and discussion

In catalytic transfer of hydrogen to substrate, it has been found that the reduction occurs by the combination of a hydride originated from formate and a proton supplied by water. The product of catalytic transfer hydrogenation of *o*-nitro anisole is *o*-anisidine. It is formed through the intermediates nitroso and hydroxylamine compound following the mechanism as shown below [6–8]:



The above mechanism prevailed during pH 6.5–7.6. Above this pH mainly at basic condition, these intermediates combine to form azoxy compound [8,9] and at acidic pH, the hydroxylamine compound forms *p*-hydroxyl *o*-methoxy amine compound. In order to detect the formation of hydroxylamine as an intermediate, the sample was immediately acidified with 3 N HCl and kept at 5 °C for 1 h. At this condition, hydroxylamine compound formed *p*-hydroxy *o*-methoxy amine [10]. This *p*-hydroxy group was detected by FTIR (Perkin Elmer Ltd., UK) near 4000 cm^{-1} as aromatic hydroxyl group.

The effect of several chemical and physical parameters on reaction rate and hence on the extent of conversion was studied. They included speed of agitation, reaction temperature, catalytic element loading, type of H-donor, its relative amount, solvents used, and reactant concentration.

3.1. Effect of speed of agitation

The catalytic transfer hydrogenation system is a heterogeneous liquid–solid system. The catalyst was in the solid form (Pd/C). At macroscopic level, the reactant, *o*-nitro anisole, diffuses from bulk of liquid to the catalyst surface and then through micro-pores of the catalyst until it reaches catalytic active centers. So is the case with H-donor, in this case ammonium formate. The reaction then takes place between adsorbed species. The H-donor decomposes to give hydride, which in turn reduces $-NO_2$ of *o*-nitro anisole to $-NH_2$. All the transport processes of substrate to the active center are in series. Thus the reactant substrate has to overcome two diffusional resistances, namely near liquid–solid interface and then intra-particle diffusion in the bulk of the catalyst. The liquid–solid mass transfer resistance depends upon the intensity of turbulence in the liquid phase, which in turn is a function of speed of agitation in the reactor. Therefore, it was thought desirable to study the effect of the speed of agitation on conversion of *o*-nitro anisole to *o*-anisidine. With the increase in speed of agitation from 300 to 1000 rpm, the extent of conversion increased from 45.2 to 100% and selectivity increased from 54.7 to 98.9%. It was observed that the speed of agitation has effect on the conversion and selectivity below 800 rpm and above this there was no effect of speed of agitation under otherwise identical conditions. Therefore, use of agitation speed more than 800 rpm ensured the absence of diffusional resistances and the reaction was confined to kinetically controlled regime. The experiments were performed at 83° C under reflux condition. In order to ascertain the absence of intra-particle diffusion, the catalyst particles of difference sizes having average particle size 30 and 85 μm were tried. The results were identical, indicating the effectiveness factor, η, was unity, the absence of intra-particle diffusion. Therefore, it was concluded that the surface reaction was the rate-controlling step in the catalytic transfer of hydrogen from formate salt to *o*-nitro anisole.

3.2. Reaction temperature

For studying temperature effect on %conversion and selectivity or rate, experiments were carried out in the temperature range 35–85 °C with 60 cm^3 solution of 1 M ammonium formate (HCO_2NH_4) as H-donor. The experimental results are

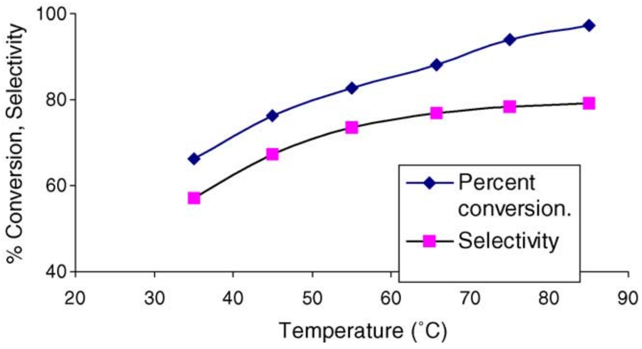


Fig. 2. Effect of change of reaction temperature on percent conversion and selectivity. Conditions—catalyst (5% Pd/C): 4% (w/w) of starting material, 1 M HCO_2NH_4: 60 cm^3, 8.2 mmol *o*-nitro anisole (OAN) in 60 cm^3 *iso*-propanol, speed: 1000 rpm and reaction time: 80 min.

shown in Fig. 2. These results were obtained after 80 min of reaction time while the amount of the catalyst was 4% (w/w) of *o*-nitro anisole. It is clear from Fig. 2 that with increase in reaction temperature, there was increase in both conversion and selectivity. At temperature of 83 °C more than 95% conversion and 75% selectivity were obtained at defined conditions. The remaining 25% intermediate was expected to be hydroxylamine compound.

3.3. Catalytic elements

To determine the suitable catalyst and its loading in the liquid phase for the highest possible yield, some experiments were carried out with three catalysts, namely, 5% Pt/C, 5% Pd/C and 5% Ru/Al_2O_3. The amount of catalyst was in the range 1.25–10% (w/w) of *o*-nitro anisole. The result indicating the effect of catalytic elements on %conversion and selectivity are shown in Figs. 3–5. It can be concluded from these observations that 5% Pd/C was better catalyst than other two in terms of both %conversion and selectivity and hence most promising. A linear dependence of the conversion on catalyst loading was observed. It is also clear that, with an increase in the catalyst loading, both %conversion and selectivity increased in every case but up to a certain limit. For 5% Pd/C when 8% (w/w) of substrate was used, more than 98% conversion with more than 99% selectivity were obtained. Above this value an increase in catalyst loading did not substantially affect the reaction yield. So we performed further experiment with the catalyst loading 8% (w/w) of *o*-nitro anisole.

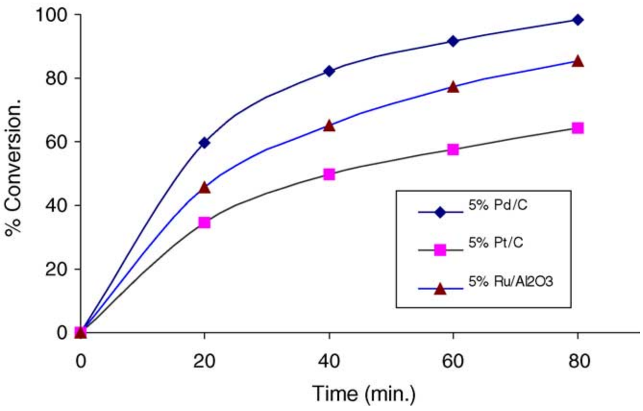


Fig. 3. Effect of catalyst element on percent conversion. Conditions—catalyst: 4% (w/w) of ONA, 1 M HCO_2NH_4: 60 cm^3, 8.2 mmol ONA in 60 cm^3 *iso*-propanol, speed: 1000 rpm, reaction time: 110 min and at 65 °C.

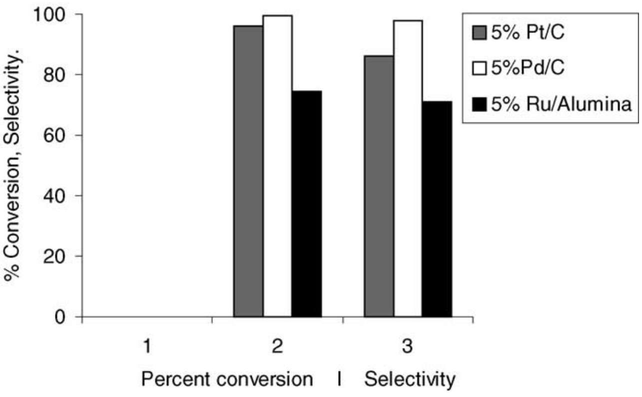


Fig. 4. Comparison of catalyst elements in terms of percent conversion and selectivity. Conditions—catalyst: 4% (w/w) of ONA, 1 M HCO_2NH_4: 60 cm^3, 8.2 mmol ONA in 60 cm^3 *iso*-propanol, speed: 1000 rpm, reaction time: 110 min and at 65 °C.

3.4. Type of formate salts

The type of formate salt is important as it affects the solubility of bicarbonate salt formed after hydrogen donation [11]. The solubility of bicarbonate salt in the reaction medium is also an important property. Thus more soluble the bicarbonate salt in the liquid medium less will be the deposition of salt particles over the catalyst surface, thereby increasing the availability of active cites for reactants only. This fact reflected on overall yield changing percent conversions and selectivity. Here experiments to determine suitable formate salt as H-donor were carried out at ∼65 °C for 110 min with catalyst (5% Pd/C) 8% (w/w) of *o*-nitro anisole and *iso*-

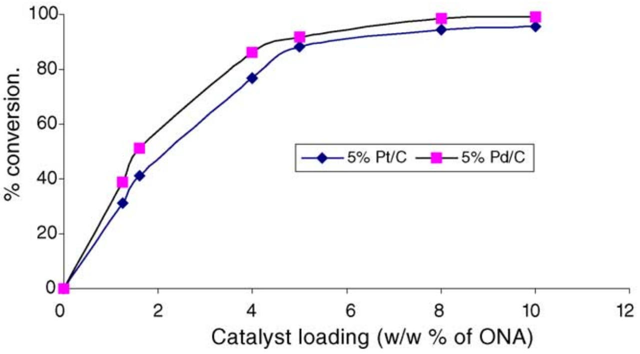


Fig. 5. Effect of catalyst loading on percent conversion. Conditions: 1 M HCO_2NH_4: 60 cm^3, 8.2 mmol ONA in 60 cm^3 *iso*-propanol, speed: 1000 rpm, reaction time: 110 min and at 65 °C.

propanol as solvent. The decomposition of HCO_2NH_4 and its H donation to promote reduction of nitro group followed the steps as shown below:

$$R\text{–}NO_2 + H_2O + HCO_2NH_4 \rightleftarrows HCO_3NH_4 + R\text{–}NH_2 \quad (1)$$

$$HCO_3NH_4 \rightarrow NH_4OH + CO_2\uparrow \quad (2)$$

$$NH_4OH \rightarrow NH_3\uparrow + H_2O \quad (3)$$

The equilibrium can be shifted towards the product side (amine) by increasing reaction temperature. When ammonium formate was used as H-donor, NH_3 and CO_2 were liberated and expelled out of the system, under given operating conditions. However, in commercial installations NH_3 can be absorbed in formic acid to produce ammonium formate for recycling thereby minimizing ammonium formate consumption (in any case, formic acid would be consumed). On the other hand, when sodium formate was used, $NaHCO_3$ remained in the system, which might mask the active centers on the catalyst resulting in sluggish reaction. A graphical comparison between formate salts (Na-formate and NH_4-formate) are shown in Fig. 6 which shows ammonium formate (HCO_2NH_4) is slightly better H-donor than HCO_2Na in both respect, percent conversion and selectivity.

3.5. *Process parameters*

The effect of the concentration of *o*-nitro anisole (ONA) on the conversion and selectivity is expected to be very complex. The catalyst affinity for various reactants have been reported as nitro-aromatics > Formate > water [9,12]. It is, therefore, obvious that for excess of any reactant would have adverse effect on the surface adsorption of the rest of species resulting in lower rate of reaction. If the product, amino compound is strongly adsorbed, we might observe adverse effect of the product on the course of the reaction. In the light of this the effect of following various process parameters was observed.

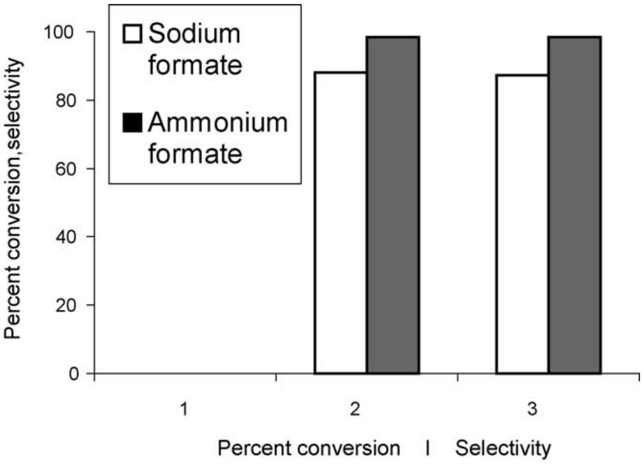


Fig. 6. Effect of nature of formate salt on percent conversion and selectivity. Conditions—catalyst (5% Pd/C): 8% (w/w) of ONA, 1 M formate solution: 60 cm^3, 8.2 mmol ONA in 60 cm^3 *iso*-propanol, agitation speed: 1000 rpm, reaction time: 110 min and at 65 °C.

Table 1
Effect of formate concentration on percent conversion and selectivity

Percent excess ammonium formate	Percent conversion	Selectivity (%)
20.1	52.0	63.9
1.6	99.6	98.6
21.9	100	99.0
27.1	100	99.1

Conditions—catalyst (5% Pd/C): 8% (w/w) of ONA, 8.2 mmol ONA in 60 cm^3 *iso*-propanol, speed: 1000 rpm, reaction time: 130 min and at 83 °C.

3.5.1. *Formate concentration*

The availability of hydrogen must affect the extent of conversion and selectivity of a hydrogenation reaction. Hydrogen availability depends on the nature of H-donor, and its concentration in aqueous solution. Depending upon the mole ratio of starting material to formate for same aqueous volume, conversion and selectivity were varied as tabulated in Table 1. Only 2% molar excess ammonium formate was adequate for complete hydrogenation of *o*-nitro anisole at 83 °C.

3.5.2. *Effect of solvent*

Dissolution of reactants and stabilization of transition state of the reaction mostly depends on nature of solvent and also its amount. To study the solvent effect on extent of conversion and selectivity experiments were carried out with three different solvents, namely, *iso*-propanol, ethanol and methanol at 65 °C. The solvents were selected on the basis of their low molecular weight and ease of availability. The catalyst 5% Pd/C of amount 8% (w/w) of starting material and aqueous 1 M HCO_2NH_4 of volume 60 cm^3, as H-donor, were used. Fig. 7 depicts the effect of solvent on the extent of conversion and selectivity. It was observed that *iso*-propanol was the best solvent studied. The better effect of *iso*-propanol as solvent may be due to its higher boiling point than the rest of alcohols. The reaction was expected to proceed at higher rates at higher temperatures. This activity can also probably

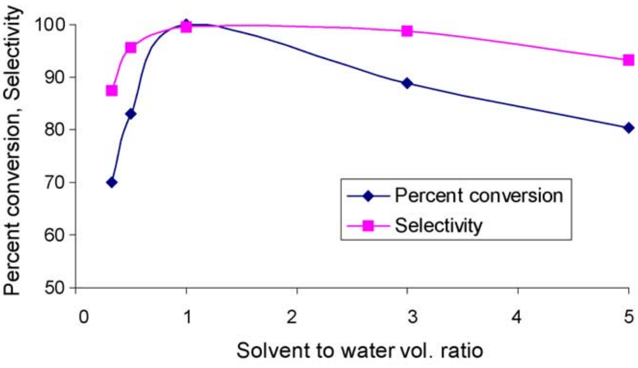


Fig. 7. Effect of solvent on percent conversion. Conditions—catalyst (5% Pd/C): 8% (w/w) of ONA, 1 M HCO_2NH_4: 60 cm^3, 8.2 mmol ONA in 60 cm^3 solvent, reaction time: 110 min and at 65 °C.

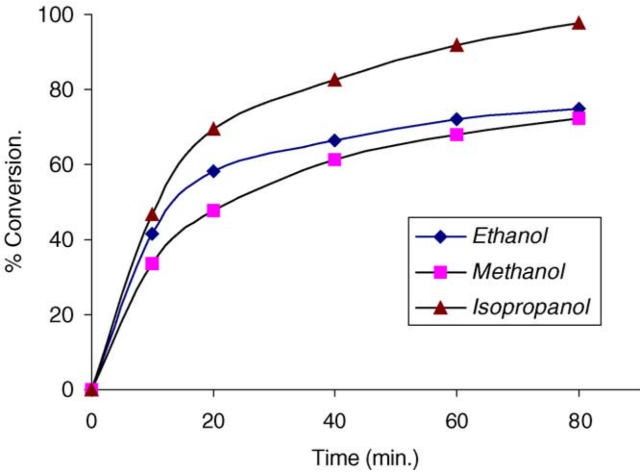


Fig. 8. Effect of solvent to water volume ratio on percent conversion and selectivity. Conditions—catalyst (5% Pd/C): 8% (w/w) of ONA, 8.2 mmol ONA in *iso*-propanol, agitation speed: 1000 rpm, reaction time: 130 min at 83 °C and 2% molar excess ammonium formate.

assigned to better stabilization of the transition state involved in reduction process. The percent conversion and selectivity depends on relative amount of water with respect to solvent present in the system. The experimental results indicate that reaction with solvent to water volume ratio 1.0 yielded maximum as shown in Fig. 8. Use of both higher and lower volume ratio so resulted in lower yield. For higher volume ratio, amount of water is insufficient for complete hydrogen donation along with HCO_2NH_4, where as higher amount of water might change adsorption behavior resulting in lower conversion.

3.5.3. Substrate concentration

Percent conversion and selectivity were measured using *o*-nitro anisole (ONA) in the range 4.1–20.5 mmol in 60 cm^3 *iso*-propanol and shown in Fig. 9. After reaction time of 110 min, it was observed that with an increase in substrate concentration (*o*-nitro anisole) both percent conversion and selectivity increased almost linearly up to 8.2 mmol of ONA then surprisingly started decreasing. At this range of substrate concentration there may present substrate inhibition effect. This was also confirmed by adding the product to a reaction mass, the conversion was less in the same time. Further, while recycling the catalyst after filtration we have observed lower activity, but when the same was refluxed with *iso*-propanol, the original activity was restored. The decrease rate for higher substrate concentration than 0.137 $kmol/m^3$ organic phase, may be due to weaker adsorption of aqueous substrate (ammonium formate and water) on catalyst surface in comparison to *o*-nitro anisole.

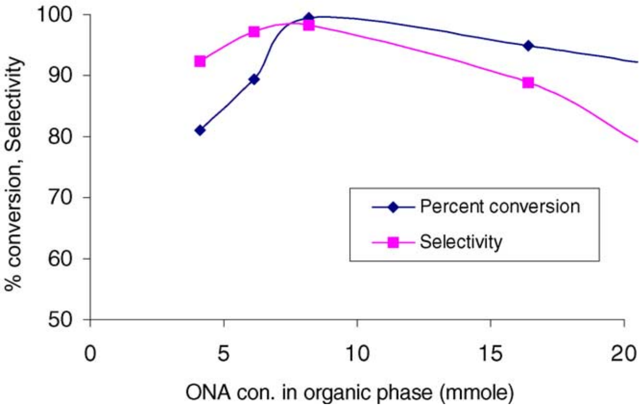


Fig. 9. Effect of ONA concentration in organic phase on percent conversion and selectivity. Conditions—catalyst (5% Pd/C): 8% (w/w) of ONA, 60 cm^3 *iso*-propanol, 2% molar excess ammonium formate, agitation speed: 1000 rpm, reaction time: 110 min and at 83 °C.

3.6. Catalyst regeneration and recycling

In order the process to become economically attractive, we should have maximum possible recycles of the catalyst or have a simple system of regeneration of the same. The first reuse of the catalyst resulted in 30% reduction in strength while second reuse resulted further 53% reduction in strength compared to the fresh catalyst. Since *iso*-propanol was the solvent medium used, it was thought to be very advantageous to use the same solvent for regeneration of catalyst activity. The spent catalyst was refluxed in *iso*-propanol for 4 h. Its original activity was completely restored after washing followed by drying.

3.7. Product separation

The product mixture (100% conversion), containing *o*-anisidine, hydroxylamine compound, if any, *iso*-propanol, formate salt and water, was extracted with toluene using volume ratio (product mixture to toluene) about 3:7. The organic layer contains the product. Product, *o*-anisidine, can be separated by recovering toluene (extractant) via distillation. Vacuum distillation of *o*-anisidine obtained from simple distillation can be used to get the product, *o*-anisidine of the desired specification.

3.8. Safety, health and environmental (SHE) aspects

Due to absence of H_2 gas the system is intrinsically safe. Further, the reaction is carried out near atmospheric pressure under reflux condition. The issue related to heat of reaction and hence heat transfer to surroundings could be safely addressed due to reflux system. The solvent, *iso*-propanol compared to methanol is less toxic and hazardous. It has flash point (−11 °C) and autoignition temperature (203 °C) [14]. The standard safety procedures need to be followed while handling *o*-nitro anisole, *o*-anisidine, formate salts and *iso*-propanol.

The catalytic transfer hydrogenation resulted in three emissions namely gaseous, solid and liquid effluent. The gaseous emission consists of NH_3, and CO_2 [15] produced after decomposition of ammonium formate, Eqs. (2) and (3).

It is possible to recover NH_3 thus produced by absorbing in formic acid and resulting ammonium formate can be recycled for catalytic transfer hydrogenation. The solid emission is by way of spent catalyst after several reuses. The spent catalyst can be sent back to the catalyst manufacturer to obtain new one at a discounted price. The aqueous raffinate stream after extraction with toluene was subjected to *iso*-propanol recovery. The bottoms containing mainly water with all contaminants having COD about 4000 ppm, was successfully treated by applying a century old Fenton chemistry [16] involving treatment of aqueous stream in a mixture at pH ∼3 with the help of $FeSO_4$ and H_2O_2 in 1 h. The reduction in COD and TOC was above 90%. A more exhaustive study is recommended in this waste treatment process. This observation demonstrated the suitability of treatment of aqueous waste stream by Fenton chemistry. The optimization of the waste treatment is excluded from the scope of this investigation.

3.9. Scale up

The scale up aspect is important in any process development. We have tried to repeat the experiment at bigger level having scale up ratio 5. For this purpose a bigger glass reactor having similar arrangement of baffles, identical impeller type and position, same impeller to vessel diameter ratio, was used at identical experimental conditions. The impeller tip speed (diameter of impeller multiplied by speed of stirring) was kept constant. This experiment resulted identical overall yield (99.6%) after the same reaction time (130 min), which is the indication of usability of scale up by tip speed criterion along with geometric similarity of impeller, baffles etc. with respect to the reactor.

4. Conclusion

The catalytic transfer hydrogenation of *o*-nitro anisole to *o*-anisidine can be carried out on Pd/C as catalyst using ammonium formate as H-donor. The solvent used was *iso*-propanol and ammonium formate was found to be better H-donor. This efficient technique provides a simple alternative to gas–liquid catalytic hydrogenation, satisfying SHE management issues. Aqueous stream treatment by simple Fenton's reagent near ambient condition yielded considerable reduction in COD and TOC.

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