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Nitrobenzene Reduction to Azobenzene using Silver loaded OMS-2

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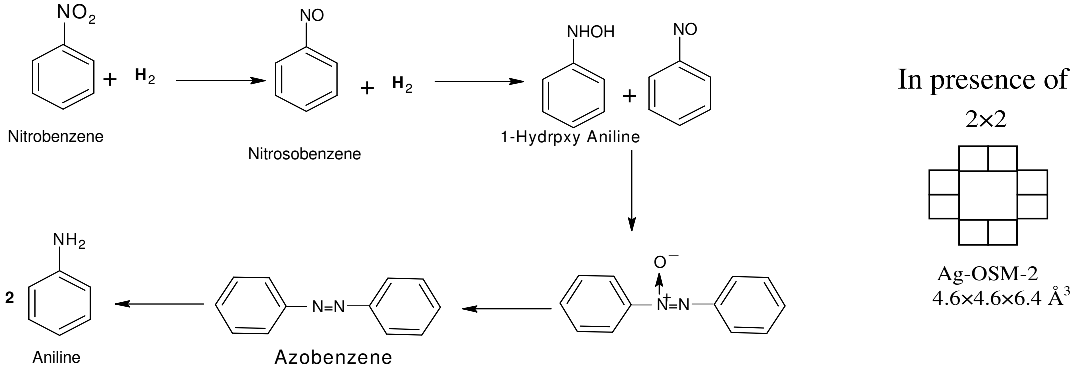
Key words: **Ag-OMS-2, azobenzene, hydrogenation, nitrobenzene, manganese oxides.**

Abstract:

Nitrobenzene reduction to aniline is a well known process with azobenzene as an intermediate product. Many azobenzene derivatives are synthesized by oxidation of aniline.

Selectivity to azobenzene during nitrobenzene reduction is very less. Aniline forms as a major product. Thus formation of azobenzene directly with high selectivity from nitrobenzene reduction can provide an economically attractive route. In the current work, this is achieved by using a silver loaded OMS-2. Catalysts with silver, with 5 to 15 (wt%), substituted OMS-2 (Ag-OMS-2) have been synthesized and used for nitrobenzene reduction. The catalysts were characterized by XRD, SEM, EDX, TGA, TPD-TPR, etc. 15% Ag-OMS-2 shows the highest conversion and selectivity for azobenzene. Study of various parameters such as catalyst loading, hydrogen pressure, nitrobenzene concentration and temperature has been studied. A suitable kinetic model was proposed. At reaction conditions of 0.0487 mol Nitrobenzene, 1.0 ml n-Dodecane, 0.005 g/cm^3 catalyst loading, make upto 50 ml with IPA, 25 kg/cm^2 H_2 pressure, 1200 rpm speed of agitation, about 39% conversion of nitrobenzene takes place with 85% selectivity towards azobenzene at 145 ^oC after 3 h of reaction. Activation energy for nitrobenzene hydrogenation to azobenzene is 14.88 kcal/mol. Thus azobenzene synthesis directly from nitrobenzene reduction using Ag-OMS-2 is an economically attractive root.

Reaction Scheme:



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1. INTRODUCTION

Hydrogenation of nitrobenzene to aniline is a commercially very important process. Aniline is used as an intermediate for the production of pesticides, dyes and other fine chemicals synthesis [1]. Azobenzene is an intermediate product, produced during the aniline production. Scheme 8.1 shows reaction path for nitrobenzene hydrogenation.

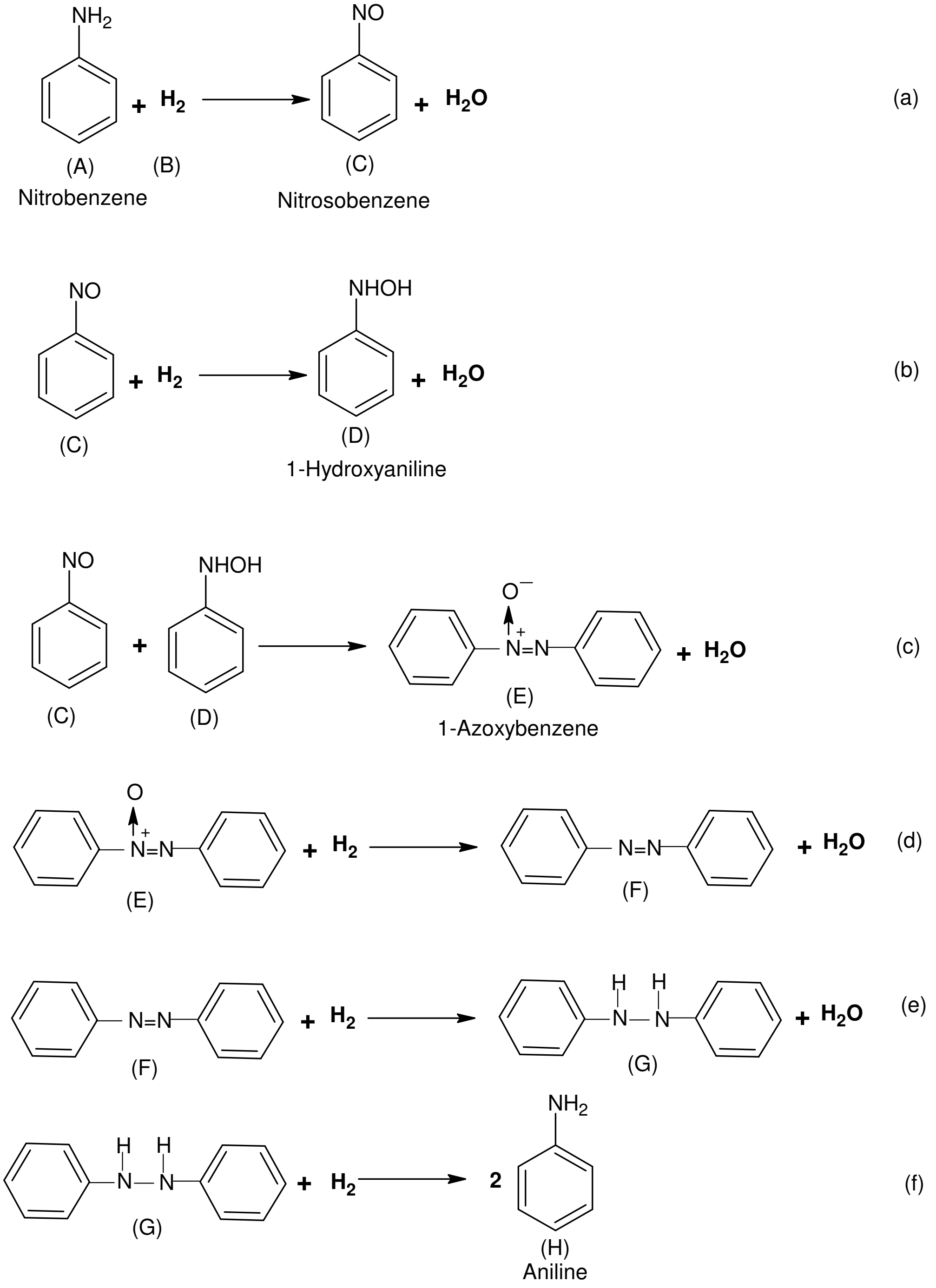

Fig. 1 Reaction Scheme of Nitrobenzene hydrogenation

Industrially azo compounds are produced by different methods like diazotization and coupling, condensation of nitro compounds with amines, reduction of nitro compounds and oxidation of amino compounds. [2]. Azobenzene and its derivatives have been utilized as organic dyes, indicators, radical reaction initiators, and therapeutic agents. In addition, azo derivatives have the potential for use in electronic and drug delivery applications [2-3]. New non-symmetrical azobenzene derivatives have been synthesized as potential molecular electronic switching device candidates [4]. Azobenzene has been prepared by many different methods. It may be obtained by the reduction of nitrobenzene with iron and acetic acid; with sodium amalgam; with alkali sulfides; with cellulose, molasses, or dextrose in alkaline solution; and by catalytic reduction. Azobenzene also results from the reduction of diazotized aniline with cuprous salts. The reduction with zinc and sodium hydroxide described also leads to azobenzene. Aniline has been oxidized to azobenzene by air and by potassium permanganate. The condensation of nitrobenzene and aniline acetate also yields azobenzene (Bigelow, H. E.; Robinson, D. B. "Azobenzene" Organic Syntheses, Collected Volume 3, p.103 (1955). All these processes are cumbersome. So a cleaner catalytic method would be most desirable.

Nitrobenzene hydrogenation has been accomplished with various catalysts containing metals such as Pd [5-6], Ni [1], Ag [7] and Au [8], which have shown very good activity towards aniline synthesis in liquid or vapor phase reaction.

Recent papers [3-4] on the synthesis of azo compounds by oxidation of amino derivatives provided a lead to us to produce the azobenzene directly from nitrobenzene. Manganese oxide octahedral molecular sieves possess an ordered array of edge and vertex shared MnO_6 molecules. Cryptomelane (OMS-2) type manganese oxide has shown good activity for various oxidation processes [9-18]. Due to the presence of Mn ions, cryptomelane (OMS-2) structure possesses very good redox properties. During oxidation reaction, catalysts shows reduction in its oxidation state from Mn^{4+} and Mn^{2+} and can be easily reoxidized to original state of Mn^{4+}, in presence of oxygen.

The current work reports hydrogenation of nitrobenzene in liquid phase using silver incorporated manganese oxide octahedral molecular sieve.

2. EXPERIMENTS

2.1. Chemicals

All chemicals were procured from firms of repute and used without further purification as follows:

Nitrobenzene, n-dodecane, methanol, iso-propyl alcohol, acetone (AR grade; M/s. s. d. Fine Chem. Ltd., India). Hydrogen gas (GC grade purity) was procured from Inox Air Ltd., Mumbai, India.

2.2. Catalyst preparation and characterization

Silver substituted manganese oxide octahedral molecular sieve **(Ag-OMS-2)** was synthesized by precipitation method under acidic conditions. Silver loading was varied from 5% to 15% (wt. percent). It was synthesized by following method. A 1.27 M manganese acetate ($Mn(OAc)_2$, $4H_2O$) solution was prepared (21 g $Mn(COOCH_2)_2$, $4H_2O$ dissolved in 67.5 ml distilled water). 8-10 ml of concentrated nitric acid was added to maintain the pH nearly equal to 1.0. A 0.5-1.05 M silver nitrate solution (x g $AgNO_3$ dissolved in 25 ml distilled water) added to the acidic solution of manganese acetate. Weight of silver was selected as per the loading of silver required in the final catalyst, i.e. 5%, 10% or 15% silver (wt. percent). A 0.37 M potassium permanganate solution (13.3 g $KMnO_4$ dissolved in 225 ml distilled water) was added drop wise to the mixture of manganese acetate and silver nitrate at 70 ^{o}C. Rigorous stirring was maintained during the addition of $KMnO_4$. The resulting mixture was stirred and refluxed at 100 °C for 24 h. The precipitate was washed several times with distilled water until pH became nearly equal to 7.0. The final product was filtered and dried at 120 °C for 10 hours and calcined at 400 ^{o}C. To compare the performance of Ag-OMS-2, OMS-2 and UDCaT-3 were synthesized by reported method [19, 20].

2.3. Catalyst characterization

Silver incorporated octahedral molecular sieves (OMS) with (2×2) type tunnel structure was synthesized and characterized with TGA, TPD, TPR, ASAP, SEM, EDX and XRD.

2.4. Reaction Procedure

Reactions were carried out in 100 ml autoclave reactor made of Hastloy C supplied by Amar Autoclaves, Mumbai, India. Temperature of the reactor was controlled with ± 1 ^{o}C accuracy using PID controller. Hydrogen gas was supplied from hydrogen cylinder at constant pressure with a two stage regulator and pressure inside the reactor was maintained with a control valve. The reactor was also equipped gas inlet and outlet ports, sampling port, rupture disc and a magnetic drive to vary the speed of agitation,.

Before starting reaction, the catalyst was dried for 2 h at 120 ^{0}C in a furnace prior to use.

Nitrobenzene hydrogenation was carried out with following reaction conditions. In a typical reaction, 1 ml n-Dodecane was added as an internal standard to 0.0487 mol of nitrobenzene and the total volume of reaction mixture made upto 50 cm^3 with iso-propyl alcohol as a solvent. To the reaction mass 0.25 g of the catalyst was added which corresponded to a loading of 0.005 g/cm^3. After completion of addition, the reactor lid was tightly closed and it was flushed with nitrogen gas followed by purging with hydrogen. Hydrogen was charged inside the reactor. Then heating was started. After attaining the desired reaction temperature, a zero hour sample was collected and the pressure of the reactor was raised to the predetermined vaule. Agitation was then commenced at 1200 rpm. Samples were withdrawn periodically and analyzed by GC.

After completion of the experiment, the reactor was cooled to room temperature and hydrogen gas was discharged. The catalyst was filtered. Fresh methanol was added to catalyst and refluxed for 2 h. After cooling it to room temperature, catalyst was filtered. Again the same procedure of washing and reflux with methanol was repeated twice. It was dried at 120 ^{o}C and re-calcined at 350 ^{o}C for 4 h.

Analysis of the reaction mixture was performed by GC on a Chemito 8610 model. A 4 m × 3.18 mm internal diameter stainless steel column packed with 10% SE-30 on chromosorb WHP was used for analysis in conjunction with a flame ionization detector. The quantification of the collected data was done through a calibration procedure by using synthetic mixtures and it was used to get conversions, rates and selectivity. Products were confirmed with GC-MS and authentic samples.

3. Results

3.1. Reaction

Scheme 1 shows that hydrogenation of nitrobenezen over Ag-OMS-2 which has mild acidic and basic sites and metal sites proceeds through a sequence of reactions. The first step is the reduction of the nitro group on the benzene ring with 2 moles of hydrogen to give 1-hydroxyaniline and water. 1-Hydroxyaniline is then converted into nitrosobenzene (C_6H_5NO) on the surface due to dehydrogenation in-situ and it is condensed on acidic sites with 1-hydroxyaniline to form azoxybenzene. Azoxybenzene is then hydrogenated to produce azobenzene. Further hydrogenation will lead to aniline. There is a need to stop this reaction at azobenzene stage.

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3.2. Catalyst screening

Fig. 8.1 shows the activity and selectivity of various catalysts used for the hydrogenation of nitrobenzene. Increasing the silver loading from 5 to 15 % by weight in the framework of the catalyst surface improves the activity and selectivity of azobenzene. 15% Ag-OMS-2 shows the highest conversion of nitrobenzene. These results confirm the synergistic effect of the silver in presence of Mn and K ions present in the catalyst. So 15% Ag-OMS-2 was selected for the further study.

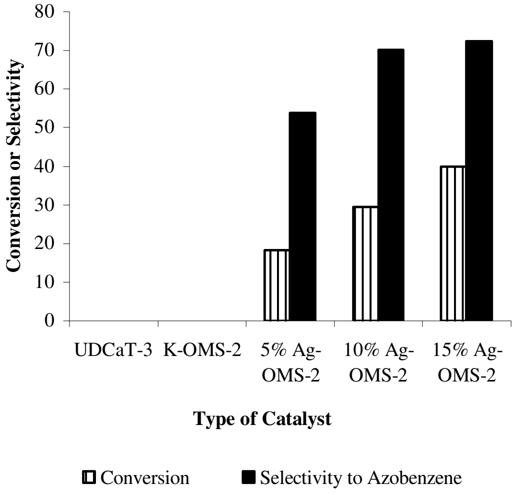

Fig. 8.1 Catalyst screening.

Reaction conditions: 0.0487 mol Nitrobenzene, 1.0 ml n-Dodecane, Make upto 50 ml with IPA, 0.01 g/cm^3 catalyst loading, 125 °C temperature, 25 kg/cm^2 hydrogen pressure, 1200 rpm speed of agitation. Results at 3rd h.

3.3. Effect of solvent

Fig. 8.2 shows the effect of various solvent on the conversion of nitrobenzene. Activity of t catalysts and conversion of nitrobenzene depends on interaction of solvent-catalyst, solvent-nitrobenzene. Acetone shows the least conversion and selectivity to azobenzene. Acetone as a solvent favors the aniline formation compared to azobenzene. Iso-propyl alcohol (IPA) gives the highest conversion of nitrobenzene to azobenzene

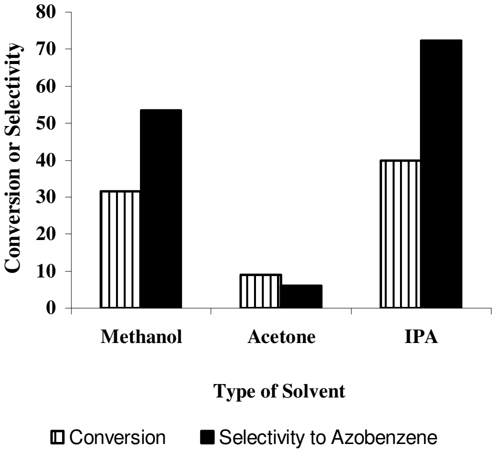

Fig. 8.2 Effect of solvent

Reaction conditions: 0.0487 gmol Nitrobenzene, 1.0 ml n-Dodecane, Make upto 50 ml with solvent, 0.01 gm/cm^3 catalyst loading, 125 °C temperature, 25 kg/cm^2 hydrogen pressure, 1200 rpm speed of agitation, 3rd hr sample

3.4. Speed of agitation and effect of external mass transfer resistance

Pure hydrogen was used and hydrogen supply was continuous to maintain constant pressure, there was no resistance associated with gas-side mass transfer of hydrogen. To find out resistance during the mass transfer of the reactant molecules from bulk liquid phase to the catalyst surface, reactions were carried out with four different speed of agitation. With increase in speed of agitation, conversion increases upto 1000 rpm. Beyond 1000 rpm there was no further improvement in the conversion level and the conversion at 1200 rpm was the same as that at 1000 rpm. This ensured that no external mass transfer resistance was present. To be on safer side, further experiments were done at 1200 rpm. The Wiesz-Prater criterion (modulus) was used to observe that it was far below unity thereby ensuring absence of intra-particle diffusion limitation.

3.5. Effect of catalyst loading

The effect of catalyst loading was studied in the range of 0.0025 to 0.01 g/cm^3 (Fig. 8.3). Conversion of nitrobenzene increased with increasing catalyst loading and the initial rates were linear in catalyst loading. No major change is observed for azobenzene selectivity. Further experiments were done with a loading of 0.005 g/cm^3.

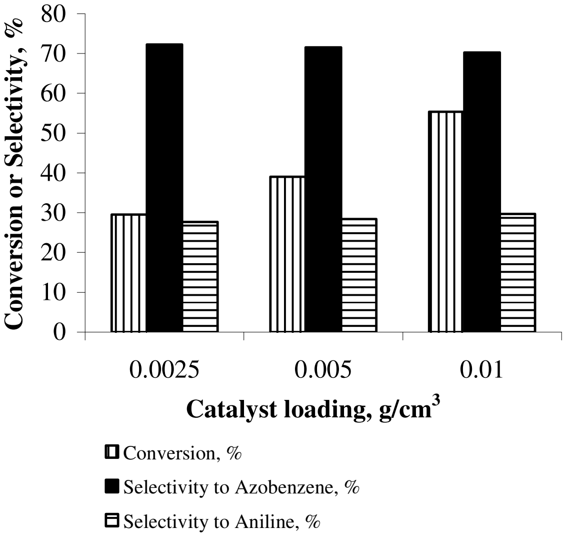

Fig. 8.3 Effect of catalyst loading

Reaction conditions : 0.0487 gmol Nitrobenzene, 1.0 ml n-Dodecane, Make upto 50 ml with IPA, 125 °C temperature, 25 kg/cm^2 hydrogen pressure, 1200 rpm speed of agitation, 3rd hr sample.

3.6 Effect of hydrogen pressure

The hydrogen pressure was varied over 25 to 45 kg/cm^2 under otherwise similar conditions (Fig. 8.4). Increase in partial pressure of hydrogen increases the conversion of nitrobenzene. However selectivity of azobenzene decreases drastically. At higher pressure azobenzene further hydrogenated to aniline due to subsequent reaction. A hydrogen pressure of 25 kg/cm^2 was selected for further study.

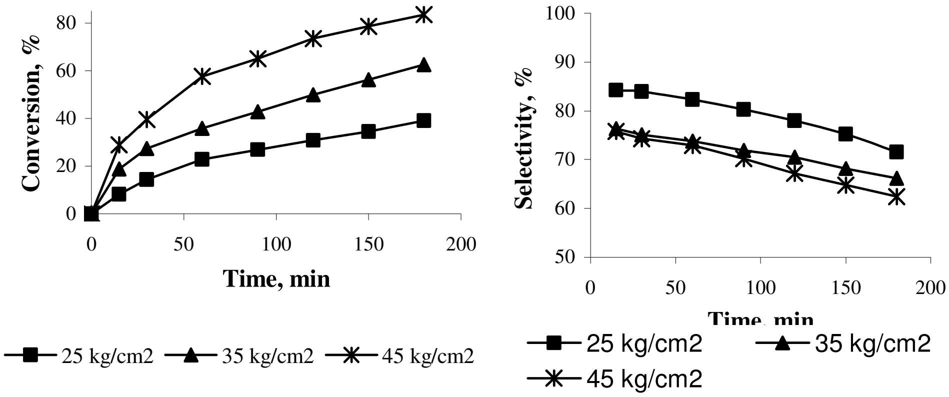

Fig. 8.4 Effect of pressure

Reaction conditions : 0.0487 mol Nitrobenzene, 1.0 ml n-Dodecane, 0.005 g/cm^3 catalyst loading, Make upto 50 ml with IPA, 125 °C temperature, 1200 rpm speed of agitation.

3.7. Effect of nitrobenzene concentration

Nitrobenzene concentration was varied from 0.4874to 1.4621 mol/lit. Conversion of nitrobenzene decreases with increase in nitrobenzene concentration (Fig. 8.5).

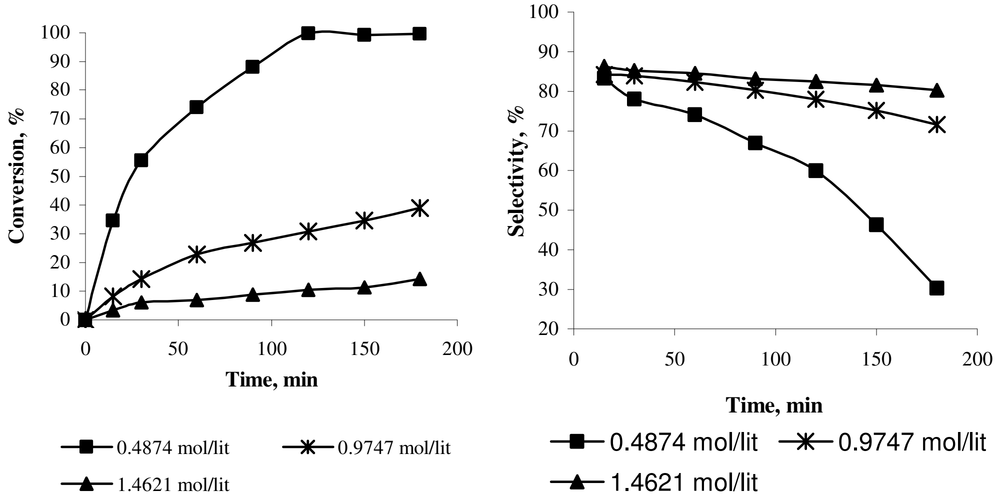

Fig. 8.5 Effect of nitrobenzene concentration

Reaction conditions: 1.0 ml n-Dodecane, 0.005 gm/cc catalyst loading, Make upto 50 ml with IPA, 125 °C temperature, 25 kg/cm^2 hydrogen pressure, 1200 rpm speed of agitation.

Selectivity for azobenzene increases with increase in concentration of nitrobenzene. Particularly at very low nitrobenzene concentration, major product formed was aniline only. And at higher concentration level conversion becomes too slow. With increase in nitrobenzene concentration, ratio of substrate to active sites increases. This leads to competitive adsorption of the molecules and rate of reaction increases but conversion of decreases. So 0.9747 mol/lit (0.0487 mol) concentration of nitrobenzene was selected for further study.

3.8. Effect of temperature

Effect of temperature was studied by varying temperature in the range of 115 to 145 °C (Fig. 8.6).

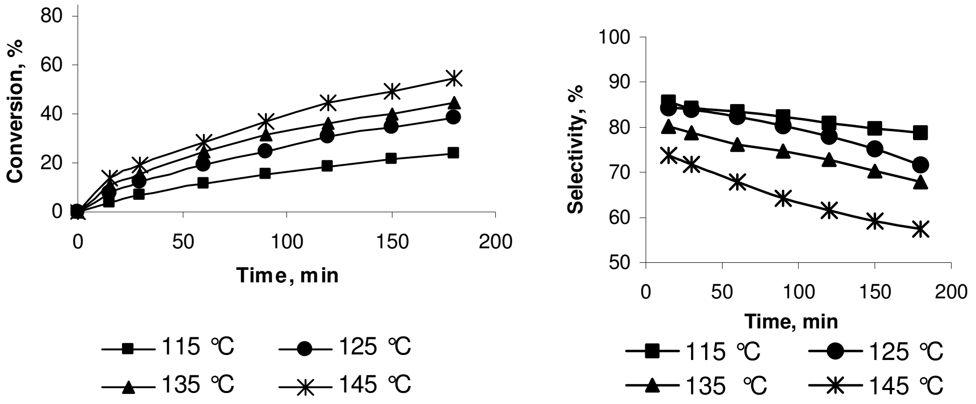

Fig. 8.6 Effect of temperature

Reaction conditions: 0.0487 mol Nitrobenzene, 1.0 ml n-Dodecane, 0.005 g/cm^3 catalyst loading, Make upto 50 ml with IPA, 25 kg/cm^2 H_2 pressure, 1200 rpm speed of agitation.

Increase in temperature increases the conversion of nitrobenzene but selectivity to azobenzene decreases whereas aniline selectivity increases.

3.9. Leaching, regeneration and reuse of the catalyst

To test if any leaching of active metal would occur, hydrogenation of aceptophenone was carried out for 1 h only. Then reaction mixture was cooled to room temperature and excess hydrogen was vented off and the catalyst was filtered from the reaction mixture. Reaction was carried out further without catalyst in the same reaction mixture. The conversions after 3 h reaction time showed that there was no change in concentration of acetophenone during reaction without catalyst. This confirms that there was no leaching of active metal during the reaction.

After completion of reaction under given conditions, the catalyst was regenerated as per procedure discussed earlier. There was no make-up of the catalyst. The conversion of nitrobenzene had decreased as catalyst activity decreases significantly. Even after second reuse catalyst activity reduces to 50% of the fresh catalysts. However selectivity of 1-phenethyl alcohol remains same.

In absence of leaching and catalyst deactivation due to heavier product formation, it was expected to have good reuseability of the catalyst. However results show a decrease in activity of catalysts with successive reuse. Catalyst itself undergoes reduction during the reaction. So this can lead to some structural changes in the catalysts. Suib (2008) proposed that hydrogen can readily reduce primarily abundant Mn^{4+} ions to Mn^{3+} or Mn^{2+}. Too much Mn^{3+} or Mn^{2+} can lead to entirely different structural types (non-tunnel systems) that are less porous materials [19]. Regeneration and re-calcination of catalysts can not restore its activity. This indicates the structural changes in the catalysts surface.

3.4. Reaction scheme, mechanism and kinetic model:

Scheme 8.1 shows the nitrobenzene hydrogenation. Reaction in the presence of Ag-OMS-2 gives azobenzene and aniline as major products with high selectivity, defined earlier. Very small (trace) amount of azoxybenzene was observed under different reaction conditions. It confirms the predicted path of nitrobenzene hydrogenation. It is assumed that reaction follows LHHW type mechanism with involvement of two sites during hydrogenation of nitrobenzene. A suitable kinetic model was developed for the predicted mechanism.

4. Conclusions

Hydrogenation of nitrobenzene over 15% Ag-OMS-2 shows good conversion and selectivity for azobenzene. Due to weak acidic and basic sites available on the surface of the catalyst, reaction stops at the azobenzene as a major product. However hydrogenation for longer time or larger catalysts loading or lower concentration of the nitrobenzene, leads to aniline as a major product. Thus synthesis of azobenzene directly from nitrobenzene hydrogenation in the presence of heterogeneous catalyst is reported for the first time. Activation energy for nitrobenzene hydrogenation in presence of 15% Ag-OMS-2 is 14.88 kcal/mol. Silver loaded octahedral molecular sieves (Ag-OMS-2) shows good activity for nitrobenzene hydrogenation with very high selectivity. However, under the reaction conditions, catalyst itself reduces and some structural changes are taking place. So catalysts reusability was very poor.

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