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HYDROGENATION OF O-NITROANISOLE CATALYSED BY Pd-C: REACTION KINETIC STUDIES IN A BATCH THREE PHASE SLURRY REACTOR

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ABSTRACT

Hydrogenation of o-nitroanisole to o-nitroanisidine is an important industrial reaction. o-nitroanisidine is a useful chemical and has application as intermediate in the manufacture of dyes and drugs. Many catalyst[1-6] have been reported in the literature but in order to selectively produce o-nitroanisidine, a modified catalyst has to be used (Pd-C). The purpose of the present paper was to investigate the reaction kinetics of hydrogenation of o-nitroanisole to o-nitroanisidine. In this work, the kinetic data was obtained using Pd (5%)-C catalyst in a stirred slurry reactor under isothermal condition. The effect of various parameters such as catalyst loading, agitation speed, initial concentration of reactant, partial pressure of hydrogen, effect of product have been investigated. The pressure vs time data were obtained over a wide range of conditions and kinetic analysis was carried out from initial rates.

Hydrogenation of o-nitroanisole to o-nitroanisidine is an interesting three phase catalytic system and providing a good example of scale up of three phase slurry reactor[7,8].

Key words: Pd-C**,** Hydrogenation, o-nitroanisole, o-nitroanisidine, Three phase slurry reactor, Catalyst.

INTRODUCTION

Hydrogenation of o-nitroanisole to get o-nitroanisidine has become important due to the application of o-nitroanisidine as aversatile chemical intermediate in the manufacture of dyes and drugs by using Lindlar type of catalyst[9].

The stoichiometric reaction is:

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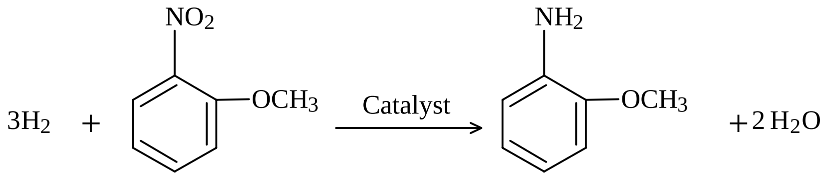

…(1)

This is a three phase reaction generally carried out in a slurry reactor. For design purpose, there is a need to study[8,10,11] the intrinsic kinetics of the above reaction using commercial catalyst and in the range of conditions used in practice. The objective of the present work was therefore to study intrinsic kinetics of selective hydrogenation of o-nitroanisole to o-nitroanisidine using Pd (5%)-C catalyst. No attempts has been made so far. Therefore the experimental work was carried out in a batch high pressure stirred reactor of 600 cm^3 capacity. In this work H_2 pressure and liquid concentration vs time data were analysed and the L-H type of rate equation has been proposed.

EXPERIMENTAL

The catalyst was prepared similar to that developed by Lindlar and Dubois in the year 1966, the physical properties of the catalyst are,

1. Catalyst : Pd (5%)-C.
2. Particle density : 2.0 g/cm^3
3. Catalyst particle diameter : 5.0×10^{-4} cm
4. Voidage of the catalyst particles : 0.90
5. Surface area : 7.70×10^4 cm^2/g.

Apparatus and procedure

Experiments were carried out in a high pressure stirred autoclave (m/s Parr Instruments) with 600 cm^3, total capacity. This equipment was provided with automatic temperature control, variable stirrer speeds and a pressure transducer with digital read out. Provision for sampling of the liquid was also provided.

A desired quantity of a o-nitroanisole was charged in the high pressure reactor along with a known quantity of catalyst. The reactor was flushed with nitrogen and a desired temperature was set. After this, the contents were flushed with hydrogen twice and pressurized to required level and then the reaction was started by switching the stirrer on. The progress of the reaction was followed by observing the change in the pressure at different times. In each run the reactant and product concentration were analysed in initial and final samples.

Some experiments were carried at the constant hydrogen pressure using a special regular between autoclave and H_2 source. The analysis was carried out by gas-chromatgraphy. A Hewlett Packard gas Chromatograph equipped with FID, an electro integrator and automatic injection facilities was used. The SS column used was 2.4 m long and packed with carbowax 20 M (5%) and carrier gas flow 6 x 10^{-5} m^3/s and injection temperature 523 K were used.

Using the procedure described above, experiments at different operating conditions were carried out. The ranges of variables covered was,

1. Catalyst loading : 0.150 x 10^{-3} to 1.0 x 10^{-3} g/cm^3
2. H_2 pressure : 7.0 to 34.0 atm.
3. Agitation speed : 9.10 to 15 rps.
4. Concentration of o-nitroanisole : 0.750 x 10^{-4} to 1.95 x 10^{-3} mol/cm^3
5. Concentration of o-nitroanisidine : 1.60 x 10^{-4} to 8.10 x 10^{-4} mol/cm^3
6. Temperature : 302 to 373 K.

RESULTS AND DISSCUSION

Hydrogenation experiments were carried out in a high pressure slurry reactor with the object of investigating intrinsic kinetics. The catalyst used in the present work was Pd (5%)-C, this is found to be highly active and selective for the reaction. The preliminary experiments indicated a material balance of about 95-98% according to the reaction (1) between hydrogen and o-nitroanisole consumed and o-nitroanisidine formed. Thus it was ensured that by using Pd (5%)-C catalyst only single reaction (1) occurred in the range of conditions investigated.

Some experiments have conducted to ascertain the reusability of the catalyst, which showed that the activity was constant even after repeated use of catalyst, Fig. 1 shows a plot of initial rate of reaction vs number of recycles. The experimental initial rates were calculated from the hydrogen pressure drop vs time data. The effect of various parameters such as catalyst loading, partial pressure of hydrogen, concentration of o-nitroanisole were studied. The results are presented in Fig. 3 and 4 respectively.

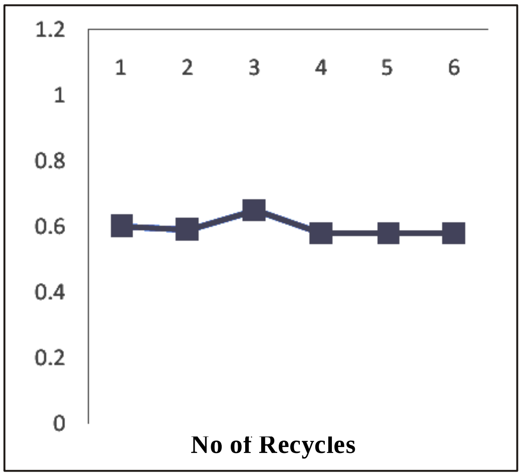

Fig. 1: Plot of initial rate of hydrogenation Vs number of recycles for catalyst loading W= 2.6 x 10 $^{-4}$ g/cm^3, o-nitroanisole concentration = 1.30 x 10^{-1} mole/cm^3, partial pressure of H_2 = 13.347 atm, T= 303 K and stirrer Speed = 15 rps

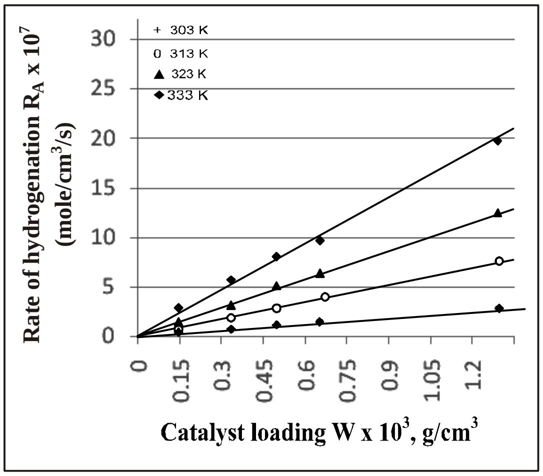

Fig. 2: Effect of catalyst loading on hydrogenation rate for stirrer Speed = 15 rps, o-nitroanisole concentration = 1.3 x 10^{-3} mol/cm^3

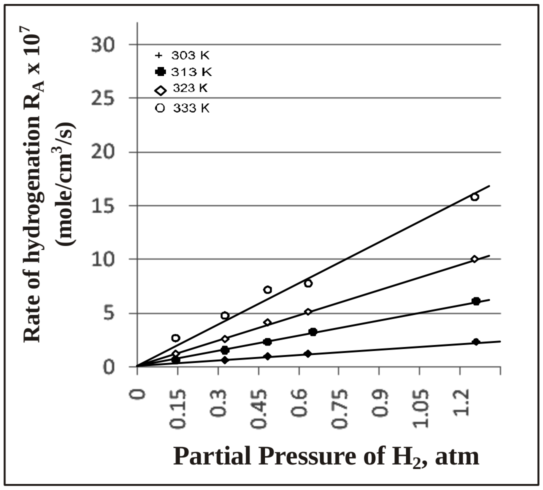

Fig. 3: Effect of pressure on initial rate of hydrogenation at catalyst conc. = 2.6 x 10^{-4} g/ cm^3 and stirrer Speed = 15 rps.

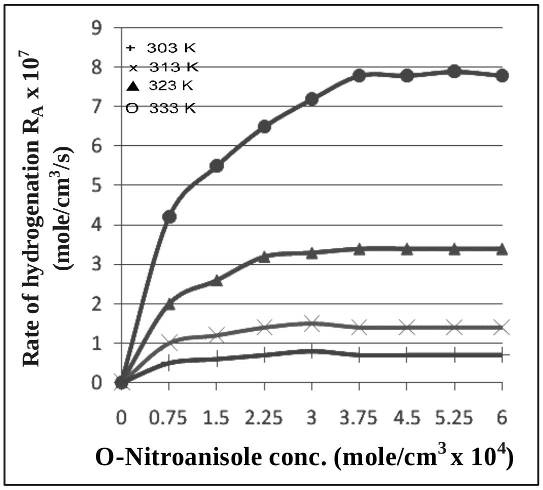

Fig. 4: Effect of o-nitroanisole conc. on initial rate of reaction at catalyst loading, W= 2.6 x 10^{-4}g/cm^3 and stirrer Speed = 15 rps

Figures 1 to 4 show he influence of various parameters on the initial hygenation rates. It was observed that at all temperatures, the rates were linearly dependent on catalyst loading. The reaction rates were independent of stirrer speed beyond 8.3 rps. The rate of hydrogenation was non-linearly dependent on concentration of o-nitroanisole with almost zero order beyond 3.27 x 10^{-4} mol/cm^3 concentration. The increase in hydrogen partial pressure increases rates with a fractional order with respect to hydrogen. The product o-nitroanisidine and water had no effect on rate of reaction. These observation indicate that a Langmuir-Hinshelwood[12,13,14] type of rate model may be applicable. For the above studies, the following form of rate equation is applicable:

$$R_A = \frac{WK\,(P_g/H_A)\,B_L}{[1+K_A(P_g/H_A)][1+K_B B_L]} \qquad \ldots(2)$$

CONCLUSION

Hydrogenation of o-nitroanisole to o-nitroanisidine was studied in a batch slurry reactor in the presence of Pd (5%)-C catalyst. The kinetic studies of hydrogenation reaction was studied in the temperature range 303 to 333 K using a high pressure autoclave. From the initial rates, a L-H type of rate expression was found to be satisfactory. The rate of hydrogenation was non-linearly dependent on concentration of o-nitroanisole with almost zero order beyond 3.27 x 10^{-4} mole/cm^3 concentration.

Increase in hydrogen partial pressure increased rates with a fractional order with respect to hydrogen. The rates were linearly dependent on catalyst loading. The kinetic equation can be used for design and scale up purposes.

Notation

B_L = Concentration of o-nitroanisole.

H_A = Henry's law constant for solubility of A.

K = Reaction rate constant.

K_A = Adsorption equilibrium constant of H_2.

K_B = Adsorption equilibrium constant of o-nitroanisole

R_A = Overall rate of reaction.

T = Temperature in K.

P_g = Partial pressure of hydrogen.

W = Mass of catalyst per unit volume of slurry

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