TRANSFER HYDROGENATION IN BATCH REACTOR OVER STRUCTURED CATALYST

Practical Chemical Reaction Engineering

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TP2.1

2025

The proposed project deals with liquid-phase transfer hydrogenation of nitrobenzenes over heterogeneous structured catalysts. You will investigate the effect of various parameters (e.g. active phase, solvent, temperature) on catalyst selectivity and activity. The reaction kinetics study is implicit as well.

MAIN TARGETS

- To get acquainted with a batch reactor operation carrying out liquid-phase catalytic reactions.
- To study the kinetics of catalytic transfer hydrogenation of substituted nitroarenes over heterogeneous structured catalysts.
- To investigate the effect of reaction conditions and catalyst nature on the catalytic response.

1.Introduction

Heterogeneously catalyzed liquid-phase hydrogenations are a class of reactions that are valuable in fine chemical industry and selective hydrogenation of a nitro-group is among them. Traditionally, functionalized anilines are produced by chemoselective hydrogenation of corresponding nitroarenes over precious metal (Pt, Pd, Ru, Rh, Au) based catalysts using gaseous H_2 as a reducing agent. The reaction network for hydrogenation of substituted nitro-benzenes is schematically presented in Fig. 1. Multiple intermediates and by-products are produced affecting the selectivity to the desired substituted aniline. Therefore, another synthetic routes are often used.

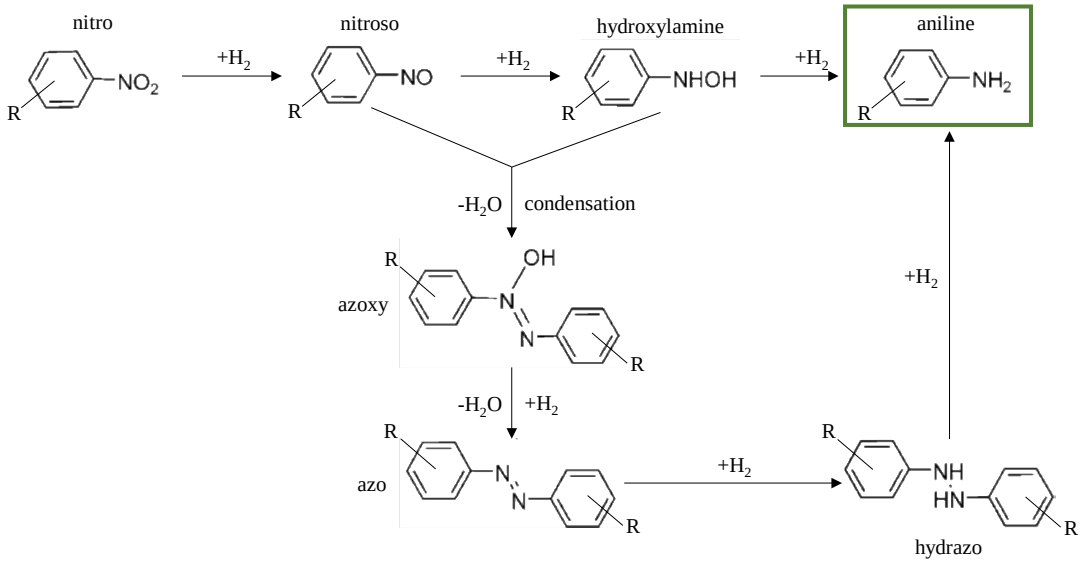

Fig 1. The proposed reaction pathway

Catalytic transfer hydrogenation is an alternative reduction method that is based on different hydrogen sources than H_2 [1], [2]. The use of liquid-phase hydrogen donors (such as hydrazine, 2-propanol, sodium borohydride, ammonium formate, etc.) allow to abandon the high pressures equipment. Significant efforts have been undertaken to replace the noble metals by abundant and much less expensive Fe, Ni, Co, etc. Since the catalytic activity of non-precious metals/metal oxides is known to be lower (as compared to noble metals), it is crucial to have them in a form of nanoparticles (NPs) providing an adequate proportion of catalytically active sites.

The process is commonly carried out in a batch or semi-batch mode.

1.1 Liquid-phase reactions on solid catalysts

During a heterogeneous catalytic process in liquid-phase, the following steps take place:
(1) mass transfer of the liquid reactants from the bulk phase to the external surface of solid catalyst;
(2) mass transfer of the liquid reactants inside the catalyst pores;
(3) adsorption of the reactants on the catalyst surface;
(4) chemical reaction;
(5) desorption of the products from the catalyst surface;
(6) mass transfer of the products inside the catalyst pores to the outer surface;
(7) mass transfer of the products from the catalyst outer surface to the bulk liquid phase.

The slowest step is the rate-determining one. If it is the external mass transport (steps 1, 7), the external mass transfer limitations govern the course of the whole heterogeneous process. If the steps 2, 6 are the slowest, the internal mass transfer influences the observed transformation rate. If one step among 3,4 or 5 is the slowest, the process is controlled by a step occurring on the surface of the catalyst. Usually adsorption and desorption are fast and reversible processes and can be considered at pseudo-equilibrium. Therefore, the step 4, i.e. the surface reaction, is the rate-determining step. Under these conditions the kinetics of catalytic reaction can be measured and the data obtained can be used for the dimensioning of eventual industrial reactor.

In summary, for obtaining reliable quantitative kinetic data, the absence of all transport limitations (heat and mass) is necessary.

1.2 Catalyst optimization

Noble metals (Pt, Pd, Rh) are known to be active and selective catalysts in transfer hydrogenation of nitro-compounds. However, significant efforts have been undertaken to replace the noble metals by much less expensive Fe, Ni, Co, etc. [3]. Since the catalytic activity of non-precious metals/metal oxides is known to be lower, it is crucial to have them in a form of nanoparticles (NPs) providing an adequate proportion of catalytically active sites. The catalytic performance can also be strongly influenced by nature of the support and the solvent used. The optimization of these process parameters is of crucial importance for achieving the highest activity/selectivity/stability.

The role of the support is one of the main factors affecting heterogeneously catalyzed processes. The support not only influences the dispersion, morphology and distribution of metal particles, but also contributes to catalysis. The specific surface area and pore size of the support control the internal diffusion limitations. Metal oxides and carbons are usually used as supports for the preparation of heterogeneous catalysts.

1.3 Intrinsic reaction kinetics

The intrinsic reaction kinetics consists of the three elementary steps of the catalytic cycle that take place on the catalytic surface: adsorption of the reactants, surface reactions and desorption of the products.
Kinetic models make the assumption that the overall reaction kinetics is the sum of elementary steps of adsorption/desorption and surface reactions.

1.4 Model reaction

Aromatic amino-compounds are often used as intermediates or reactants in a range of chemical productions. They are applied in the manufacture of pharmaceuticals (p-aminophenol and o-, m- and p-toluidine), polymer and dyestuffs (m-phenylenediamine and m-nitroaniline), pesticides and herbicides (3,4-dichloroaniline). Aniline (AN) is used in the production of rubbers, dyes and amino resins.

p-Chloronitrobenzene (p-CNB) has been chosen as a model reactant for the present TP. Selective hydrogenation of this compound yields p-chloroaniline (p-CAN), an important intermediate in multiple industrial applications. During hydrogenation of halonitrobenzenes, the main problem is a cleavage of the halo-group from the aromatic ring (see Fig. 2). It has been shown that this C-Cl scission can be influenced by active metal nature, metal dispersion, catalyst support, and by additives. The addition of a second metal to the active phase is one of the most effective ways of influencing the selectivity, activity and stability of the catalyst.
A range of activity/selectivity responses on temperature, pressure, reaction time, and reactant(s) concentration changes are already documented in the literature for different catalytic systems. However, comprehensive and systematic kinetic and mechanistic studies are still required.

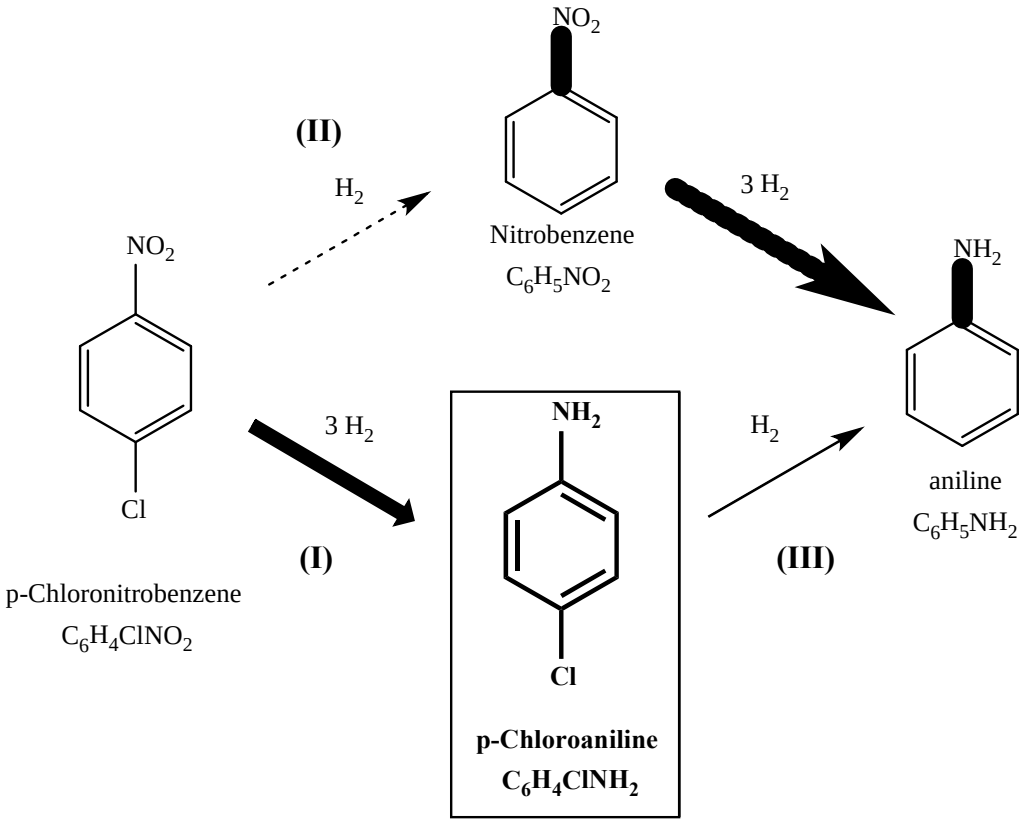

Fig 2. Reaction pathways for the hydrogenation of *p*-CNB to *p*-CAN. The targeted route is represented by solid arrow

1. R. A. W. Johnstone, A. H. Wilby, I. D. Entwistle, *Chem Rev*, **85** (1985) 129-170.
2. G. Brieger, T. J. Nestrick, Chem Rev, **74** (1974) 567-580.
3. H. U. Blaser, H. Steiner, M. Studer, *ChemCatChem*, **1** (2009) 210.

2. Objectives

- *To get acquainted with a semi-batch reactor operation carrying out liquid-phase catalytic reactions.* You will learn how to perform the reaction in an autoclave, to determine the presence/absence of mass transfer limitations, to choose the reaction conditions corresponding to kinetic regime.

- *To study the kinetics of selective catalytic hydrogenation of substituted nitroarenes over heterogeneous structured catalysts.* You will determine kinetic parameters such as activation energy, reaction orders, etc.

- *To investigate the effects of reaction conditions and catalyst nature on the catalytic response.* The effect of various parameters (such as catalyst nature, solvent, stirring intensity, temperature, etc.) on catalyst activity/selectivity will be studied. The basic knowledge should be applied to explain the observed effects.

- *To get the concepts* for catalyst synthesis and product characterization.

3. Experimental

3.1 Catalysts

Metal oxide (Fe_2O_3, Co_3O_4) based catalysts were prepared by deposition of the precursors ($M(NO_3)_x \cdot aq$) on activated carbon fibers (ACF) support. This support, consisting of arranged microfilament (d-20 μm), avoids internal mass transfer limitations within micro-sized filaments[1]. Metal oxide nanoparticles confined within ACF pores were synthesized by a thermal decomposition of the precursor at 350-500°C under inert atmosphere (N_2). Available catalysts are listed in Table 1. Remember that the loading is expressed on a metal basis and not on a metal oxide basis.

Fe_2O_3	Co_3O_4
1.8%	2%
6.2%	6.5%
9.5%	10%
16.6%	17.3%

Table 1: List of the metal oxides supported on ACF. Loadings are expressed as wt.% of the metal refered to the total weight of the catalyst.

3.2 Experimental setup

A commercial semi-batch stirred stainless steel reactor (150 cm^3 autoclave, Büchi AG, Uster, Switzerland) equipped with 4 wall baffles is schematically presented in Figure 3.

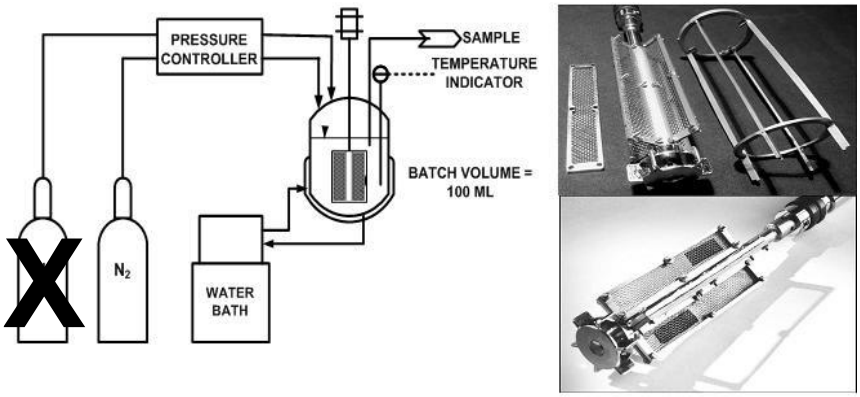

Figure 3. Experimental setup to study a liquid-phase reaction

A stainless steel 4-blade disk turbine impeller (equipped with a self-gassing hollow shaft) provides effective agitation up-to 1500-2000 rpm. Catalyst is fixed on 4 wire meshed blades attached to the stirrer shaft. An oil bath circulator is used to control the reaction temperature. The reactor is connected to a nitrogen line and to a vent connected to the back of the fumehood. Pressure is measured by a manometer.

[1] Beswick, O.; Parastaev, A.; Yuranov, I.; LaGrange, T.; Dyson, P. J.; Kiwi-Minsker, L. *Catalysis Today* **2017**, *279*, 29–35.

3.3 Experimental procedure

Prepare the reaction solution

- Weigh ~ 1.0g of *p*-CNB and 1.0g of m-xylene, add the solvent (ethanol). Total volume is 100ml. Dissolve under stirring.
- Cut and weigh ~0.2 of the catalyst. Fix it onto the stirrer.
- Write down the weights.

Prepare the reactor

- Switch on all the control modules.
- Fix the stirrer (you should here a "click").
- Put the solution into the reactor and close it.
- **Start stirring,** there should be no noise.
- Purge the reactor with nitrogen
  open the nitrogen valve;
  close the nitrogen valve;
  wait for a few seconds;
  stop stirring;
  release the pressure by opening the outlet valve;
  start stirring again;
  repeat the procedure 3 times.

!! Be careful!! If the stirring is on during pressure release, some liquid will be sent to the vent line.

Heat up the reactor (should be done under stirring)

- Switch on the heating bath.
- Open the cooling water system
- Set the temperature (2-3°C higher).

Start the reaction

The following steps should be done quickly.

- Check that stirring is ON.
- Make sure temperature is stable at the set point
- Inject hydrazine hydrate solution in water (24-26%) (4ml)
  !! This is a critical step as hydrazine is a toxic compound. Also, pressure in the reactor can be relatively high!!

  Do not stop stirring.
  Fix the syringe on the sampling tube.

Open the valve **(Hold the syringe! Pressure!).**
Inject hydrazine
Wash the syringe and sampling tube by pumping (3 times)
Close the valve

- Start the timer (just after injection)

Stop the reaction

- Set the oil bath to the lowest temperature possible (-20°C).
- Increase the stirring to accelerate cooling down.
- When temperature is ~40°C, stop the stirring, release the pressure and open the reactor.

Clean the reactor

- Take out the stirrer with the catalyst, wash it by ethanol, and wash the lower and upper parts of the reactor by ethanol.
- Dry it by an air flow.

Sampling

Samples should be withdrawn regularly. The first sample should be taken just before the reaction start (before the injection of hydrazine). The number of samples depends on the reaction and should be discussed with the assistant.

!!! Be careful, the pressure in the reactor can be relatively high. Wear glasses and lab coat!!!

- **Do not stop stirring.**
- Fix the syringe on the sampling tube.
- Open the valve **(Hold the syringe! Pressure!).**
- Wash the syringe and sampling tube by pumping (3 times), fill up the syringe (0.2 ml is enough!)
- Close the valve.
- Read the **sampling time**.
- Put the solution into a GC vial.
- Dilute by ethanol.

3.4 Analytics

The reaction progress is monitored and the reactants/products concentrations are measured by GC. Small samples of the reaction mixtures are periodically withdrawn and GC analysis is performed using Clarus (Perkin Elmer) equipped with a 30 m Stabilwax (Crossbond Carbowax-PEG, Restek, USA) 0.32 mm capillary column with a 0.25 μm coating. The carrier gas is He. All components are assumed to have the same GC-response factors.

4. Detailed plan of manipulations

The "concentration versus time" profiles should be presented for each reaction component.

As a measure of activity, the initial reaction rate should be calculated (per unit of catalyst and/or active phase.

$$r = \frac{mol_{pCNB}}{s \,.\, mol_M}$$

Selectivity (integral selectivity), yield and conversion should be calculated. These results could be presented as plots of "Selectivity to *p*-CAN vs. *p*-CNB conversion" and "*p*-CAN yield vs. p-CNB conversion".

The following plan of manipulations is proposed:

A. Preliminary tests.

In a series of blank tests you will carry out the reaction in the absence of the catalyst. The support without the active phase should be tested as well.

B. Diffusion limitations with the structured catalyst.

The structured catalyst should be tested under the reaction conditions in terms of external and/or internal diffusion limitations. Once a kinetic regime is found, the reaction kinetics can be studied.

C. Determination of kinetic parameters.

The apparent activation energy should be determined under a kinetic regime by varying the reaction temperature between 313 K and 368 K.

The reaction rate should be measured at different substrate concentrations (under excess of hydrazine) and the partial order toward *p*-CNB should be found.

D. Influence of solvents on the catalyst behavior.

The influence of solvents on the catalysis should be studied. Ethanol, iso-propanol and methanol could be used.

E. Influence of catalyst loading and species of metal nanoparticle

The catalyst with different metal loadings should be tested under the same condition to determine whether loading affects the reaction rate or not. Different metal catalyst should also be tested for comparison.

F. Stability of the catalyst

The optimized catalyst should be subjected to several consecutive runs in order to evaluate its stability.

APPENDIX I – LIST OF CHEMICALS AND SAFETY CONSIDERATIONS

Name	Chemical formula	Form	Danger
p-chloronitro-benzene (pCNB)	$C_6H_4ClNO_2$	Solid	
Ethanol	C_2H_6O	Liquid	
Isopropanol	C_3H_8O	Liquid	
Methanol	CH_4O	Liquid	
Hydrazine	N_2H_4	Liquid	

For all manipulations, you need to wear safety equipment composed of safety glasses, nitrile gloves and lab coat.