Abstract

ABSTRACT OF THESIS

Studies on mono-, bi-metallic and nano catalysts of nickel, palladium and platinum metals and their applications in selective hydrogenation of acetylenic compounds and nitroaromatics of industrial relevance

Catalysis has been playing a major role for last few decades due to its wide range applications in various fields such as fuel cell as renewable source of energy, abatement of air pollution, waste water treatment, environmental protection by developing green processes. In particular, due to increasing awareness of environmental issues, chemical industries look for the cleaner, safer, environmentally acceptable alternative and sustainable processes. Chemical processes should have minimum waste generation, improved product quality and cost effectiveness. Traditionally, for manufacturing fine chemicals the synthetic organic chemists used the classical ‘stoichiometric’ routes, which generate large amount of organic or inorganic wastes in the range of 1-100 kg byproduct formed per kg of product, which gives serious impact on environment and hence on human life. Some of the well known examples of such processes are oxidations with permanganate and chromium compounds, reductions with metal acids and metal hydrides, halogenations, alkylation, nitration etc. These processes are now being replaced by catalytic routes and among these processes, catalytic hydrogenation reactions of various organic functional groups is one of the core technologies widely used in chemical industries. Although hydrogenation is supposed to be a well developed subjected area, there is a great deal that can be still done for fundamental understanding particularly, in designing new catalysts and routes for selective hydrogenation reactions of industrial relevance [1].

For this purpose, we undertook a detailed study on the preparation and characterization of mono-, bimetallic and nanocatalysts using nickel, palladium and platinum metals. These catalysts were evaluated for their activities for the selective hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol and butane-1,4-diols, phenylacetylene to styrene, nitrobenzene to \( p\)-aminophenol, \( m\)-chloronitrobenzene to \( m\)-chboroaniline.
Abstract

Catalytic hydrogenation of acetylenic compounds e.g. 2-butyne-1,4diol and phenylacetylene is an industrially important reaction whose end products 2-butene-1,4 diol and styrene respectively are widely used in the manufacture of endosulfan (insecticide), tetrahydrofuran, vitamins A and B₆ and in polymer industries. Since, hydrogenation of 2-butyne-1,4diol and phenylacetylene involve consecutive as well as parallel reactions, controlling the selectivity to olefinic products is a challenging task. Several catalysts were reported for selective semi-hydrogenation of acetylenic compounds[2], however the major drawbacks associated with these catalysts are poor activity in subsequent reuses, and moreover, such processes require the complete removal of the additives for obtaining highest purity of the product for its end uses in the fine chemical or pharmaceutical sector. The noble metals such as palladium, ruthenium alone or in combination with other metals such as zinc, lead, cadmium, copper, and/or organic amines were also used as catalyst systems to improve selectivity to the intermediate, B₂D₃[3-9].

Hydrogenation of various nitroaromatic compounds is also a commercially important process and in the present thesis we have studied the following reactions (i) single step direct hydrogenation of nitrobenzene to p-aminophenol (PAP), with a particular emphasis on intermediate p-phenylhydroxylamine formed and its rearrangement to PAP and (ii) selective hydrogenation of m-chloronitrobenzene to m-chloroaniline, without/minimum dehalogenation [10]. Both these are multi step processes involving Fe/HCl reduction (Bechamp Process) which produced equivalent or higher amount of Fe-FeO sludge as a byproduct. The catalytic hydrogenation using supported metal catalysts is an excellent alternative to the conventional Bechamp process which gives better yield and selectivity to the desired products [11,12].

OBJECTIVES OF THE PRESENT INVESTIGATION

- Preparation of colloidal, bulk and nano structured supported mono, and bi-metallic catalysts involving various transition metals such as Ni, Pd, Pt.
Abstract

• Physico-chemical characterization of the prepared catalysts by various techniques such as powder X-ray diffraction, SEM, EDAX, BET surface area, Raman, FTIR, Chemisorption, XPS.
• Standardization of analytical methods for the model reaction systems investigated using GC and HPLC.
• Activity testing of the prepared catalysts for selective hydrogenation of 2-butyne-1,4-diol, phenylacetylene, nitrobenzene and m-chloronitrobenzene, in high pressure batch and continuous reactors.
• To study the kinetics of formation and further rearrangement of an intermediate phenylhydroxylamine in hydrogenation of nitrobenzene to PAP.
• To study the role of additives on extent of dehalogenation in hydrogenation of m-chloronitrobenzene to m-chloroaniline
• Optimization of reaction parameters such as temperature, pressure, catalyst and substrate loading in order to achieve highest conversion and selectivity, for all the hydrogenation reaction studied in this work.
• To correlate the observed activity and selectivity patterns with the catalyst characterization data.

OUTLINE OF THE THESIS

The thesis contains total 7 chapters among which the first two chapters include general introduction including objectives and experimental techniques respectively. The scientific results are then divided in two parts viz. Part I dealing with selective hydrogenation of acetylenic compounds and Part II contains hydrogenation of nitroaromatic compounds. A brief summery of the thesis is outlined here.

Chapter 1 presents general introduction to catalysis, classification of heterogeneous catalysts, and reduction methods. At the end of this chapter, the scope and objectives of this thesis are given.
Chapter 2 includes preparation details for various types of mono and bimetallic catalysts such as Pt/C, Ni/C, Ni-Pt/C, colloidal Pd and supported nano catalysts, synthesis of carbon nanotubes, Pd functionalization of carbon nanotubes and experimental setup and procedure for hydrogenation reactions in batch and continuous reactors under high and atmospheric pressure conditions. Details of catalyst characterization techniques used such as FTIR, BET N\textsubscript{2} adsorption, Chemisorption, XRD, Raman, XPS, SEM, TEM and the analytical techniques such as GC and HPLC are also included.

Chapter 3 contains specific literature survey on hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol and butane-1,4diol and activity results of supported palladium nanoparticles, Pt/CaCO\textsubscript{3} and Pd-functionalized carbon nanotubes (CNTs) on this hydrogenation systems.

Continuous hydrogenation of 2-butyne-1,4-diol (B\textsubscript{3}D) in presence of 1% Pt/CaCO\textsubscript{3} catalyst in a fixed-bed reactor gave 2-butene-1,4-diol (B\textsubscript{2}D) and butane-1,4-diol (B\textsubscript{1}D) without formation of any other side products. In case of continuous hydrogenation, higher selectivity (66%) to B\textsubscript{2}D was obtained and the selectivity pattern was completely different from that found in case of batch slurry operation in which B\textsubscript{1}D selectivity was very much higher (83%) than the B\textsubscript{2}D selectivity (17%). The selectivity ratio of B\textsubscript{1}D to B\textsubscript{2}D could be altered by varying the H\textsubscript{2} pressure, temperature, liquid and gas flow rate conditions at the reactor inlet. A theoretical model was also developed incorporating the conditions of external and intraparticle mass transfer, partial wetting of the catalyst using reaction kinetics of 2-butyne-1,4-diol hydrogenation in a batch slurry reactor. The reactor model was validated by carrying out hydrogenation experiments under various reactor inlet conditions. The predictions obtained by the proposed reactor model was found to agree well with the experimental data over a wide range of operating conditions [13].

Another interesting study included in this chapter is activity and selectivity behavior of supported palladium nanoparticles. Pd nanoparticles supported on activated carbon and CaCO\textsubscript{3} showed the higher activity (9-21 times) and selectivity towards B\textsubscript{2}D (> 99%) than the bulk Pd/C catalyst prepared by conventional method for 2-butyne-1,4-diol. The pulse titration study showed that metal dispersion for the nano catalyst was > 65% higher than that for the bulk catalyst [14]. Performance of Pd-functionalized carbon nanotubes
Abstract

(CNTs) for the hydrogenation of 2-butyne 1, 4 diol was also studied. Pd-functionalized carbon nanotubes catalyst was prepared by supporting Pd on acid-treated carbon nanotubes. Pd-functionalized carbon nanotubes showed higher selectivity (93%) to 2-buten-1, 4-diol than Pd supported on commercial carbon (70% selectivity to 2-buten-1, 4-diol) with complete conversion of 2-butyne-1, 4-diol. Pd/CNTs catalyst was characterized by BET, FTIR, Raman, XRD, EDAX, ICP-OES, SEM and TEM analysis. The reusability of the catalyst was evaluated by the catalyst recycle experiments [15].

Chapter 4 deals with literature survey and activity results of colloidal Pd nanoparticles on hydrogenation of phenylacetylene. Colloidal Pd nanoparticles prepared by chemical reduction method using PVP as a capping agent showed 3.5 times higher reaction rate than the bulk catalyst for hydrogenation of phenylacetylene under milder reaction conditions. Effect of temperature and pressure was also studied to achieve the complete conversion and high selectivity to styrene. At 90% conversion of phenylacetylene, selectivity to styrene was found to be 90% which decreased to 68% for complete conversion of phenylacetylene. This is due to formation of ethylbenzene by further hydrogenation of styrene.

Chapter 5 contains literature survey and catalyst activity results of Pd/C catalysts on direct hydrogenation of nitrobenzene to \( p \)-aminophenol (PAP). The mechanistic pathway for hydrogenation of nitrobenzene to PAP involves two-steps (i) reduction of nitrobenzene to give phenylhydroxylamine (PHA) as an intermediate (ii) Bamberger rearrangement of PHA in presence of an aqueous acid to give PAP. Formation of aniline via further hydrogenation of PHA is a major competing reaction affecting the selectivity to PAP. Catalytic hydrogenation of nitrobenzene using 3% Pt/C catalyst at 303 K showed 95% selectivity to PHA at 36 % conversion of nitrobenzene which decreased to 75% for complete conversion of nitrobenzene due to the formation of aniline as a byproduct. Rearrangement of PHA in an inert atmosphere (Ar) gave a higher selectivity (77%) to PAP as compared to the rearrangement carried out under hydrogen atmosphere.

Another part of this chapter includes the study on optimization of reaction conditions and scale up of this important industrial hydrogenation system. The downstream process step
of neutralization of the reaction crude was also fine tuned in order to achieve the highest selectivity to p-aminophenol (75% isolated yield of PAP).

Chapter 6 contains literature survey and activity testing of the mono, bi-metallic catalysts containing Pd, Ni metals for selective hydrogenation of m-chloronitrobenzene to m-chloroaniline. In this work, we studied the role of an additive, sodium carbonate reducing the extent of dehalogenation to give 94% selectivity to m-chloroaniline. It was also found that the Ni-Pt based bimetallic catalysts showed high activity and almost complete selectivity (>99%) towards m-chloroaniline compared with Ni based monometallic catalysts.

Chapter 7 summarizes work presented in all the chapters and general conclusions arrived at from the discussed results.

Reference


