Eurasian ChemTech Journal 2 (2000) 101-105

Hydrogenation of Aromatic Nitrocompounds on Supported Mono- and Bimetallic Catalysts

A.T.Massenova* and L.R.Sassykova

D.V.Sokolsky Institute of Organic Catalysis and Electrochemistry,

142 Kunaev St., 480100 Almaty, Kazakhstan

Abstract

Catalytic hydrogenation of substituted aromatic nitrocompounds and hydrocarbons has been studied. It was established that monometallic Pd-catalysts were suitable for reduction of nitrogroups. Bifunctional catalysts such as Rh-Pt, Rh-Pd, Pd-Ru and Rh-Ru were used for hydrogenation of both aromatic ring and nitrogroup and sequence of their hydrogenation depended on support nature. Over Rh-Pt alumina supported catalysts consequent hydrogenation of NO_2 and benzene ring took place, over silica supported catalysts their consecutive hydrogenation was observed. Such catalytic properties of bimetallic Rh-Pt and Rh-Pd catalysts probably connected with metal-metal interaction leading to optimal adsorption strength of uniformly adsorbed hydrogen. The optimal reaction conditions (temperature and hydrogen pressure) have been elaborated for synthesis of alicyclic amines with 95-99% yields.

Introduction

Reduction of aromatic nitrocompounds is very important industrial process as its products - amines are used for production of pharmaceuticals, dyes and different fine and specialty chemicals. Traditionally aromatic amines are mostly produced by non-catalytic synthesis such as stoichiometric reduction of nitrocompounds by Fe powder or alkali metals sulphides. The main difficulties of that processes are the formation of at least more than 20 times wastes besides desirable products, the problem of after-treatment of by-products, low process selectivity. The catalytic method of nitrocompounds hydrogenation is the most attractive because of high effectiveness and selectivity which provide high yields of pure products - the main requirement especially for medicines.

Mostly the catalytic hydrogenation of aromatic nitrocompounds to aromatic amines [1,2] was well studied using the catalysts on the base of Pd. The hydrogenation of benzene ring of aromatic amines to alicyclic amines was also investigated but not so wide as nitrogroups [3,4]. And very less studies were devoted to hydrogenation of aromatic nitrocompounds to alicyclic amines [5,6]. So the objectives of present work are to study the joint process - hydrogenation of both nitrogroup and benzene ring of aromatic nitrocompounds and to develop the active and selective catalysts for this process. For this purposes we studied:

1). hydrogenation of nitrogroup of different substituted nitrocompounds such as nitrobenzene, o-,p-nitrophenols, o-, p-,m-nitroanilines, 1-p-nitrophenyl-2-amino-1,3-propandiol to aniline, o,p- aminophenols, o-, p-, m- phenylendiamines, 1-p-aminophenyl-2-amino-1,3-propandiol respectively;

2). hydrogenation of benzene ring of aromatic hydrocarbons - benzene, ethylbenzene, cumene to cyclohexane, ethylcyclohexane and iso-propylcyclohexane;

3). hydrogenation of both nitrogroup and aromatic ring - nitrobenzene and dinitrodibenzo-18(24,30)-crown-6(8,10) ethers to cyclohexylamine and diaminodicyclohexyl-18(24,30)-crown-6(8,10) ethers.

It is very important to carry out these processes at mild conditions because amines are thermally unstable substances and also for energy saving. So the elaboration of optimal conditions such as the temperature, hydrogen pressure and solvent selection are also necessary.

Experimental

The catalysts on the base of Pd, Rh, Pt and Ru (both

---

*corresponding author. E-mail:adm@orgcat.academ.alma-ata.su mono- and bimetallic) were prepared by alumina or silica impregnation and co-impregnation with aqueous solutions of corresponding salts. For the catalysts characterisation XRD (XR-Diffractometer «Philips» 1140, 2q=10-70^{o}), SEM(«Hitachi»,S-250, 10KV), TPD (GDTD-24AB,»Setaram»), BET (nitrogen adsorption, «Accusorb») methods were used. The hydrogenation reaction was carried out in an autoclave (volume 100 cm^{-3}) at isobaric and isothermal conditions and external kinetic band. Hydrogenation reaction has been studied at temperatures 293-373K and hydrogen pressures 0.5-12.0 MPa. For aromatic nitrocompounds hydrogenation ethanol, iso-propanol, THF, benzene and water were used as the solvents. The hydrogenation of aromatic hydrocarbons was carried out without solvent. Gas-liquid chromatography, IR-spectroscopy and diasometric titration were used as the methods for analysis of organic compounds.

Results and discussion

1. Hydrogenation of nitrogroup

Pd is known to be the best catalyst for nitrogroup hydrogenation[1,2]. Therefore we used 0.5-5.0% alumina supported Pd catalysts which have shown the highest activity and selectivity in preliminary investigation on hydrogenation of different substituted aromatic nitrocompounds. Alumina was selected as the best support as compare to SiO$_2$, C and MgO.

Nitrobenzene, o- and p-nitrophenols, nitroanilines were selectively hydrogenated on Pd/alumina with the yields of aniline, phenylendiamines and o-,p-aminophenols equal to 95-99%.

Effect of temperature, hydrogen pressure and solvents on the reaction rate and yield of desired products has been studied.

Temperature and hydrogen pressure increased the hydrogenation rate and the yields of amines for all nitrocompounds. But rate didn't increase reaching the definite «limit» hydrogen pressure which depends on substrate nature: for nitrobenzene – 12.0 MPa, for nitrophenols – 9.0 MPa. In studied temperature interval we calculated the activation energies from the plot of log dr/dt vs 1/T using Arrhenius equation.

Reaction rate for different nitrocompounds decreases by sequence which is in good correlation with the activation energies:

nitrobenzene (20 KJ/mol) > p-nitroaniline (20) >
m-nitroaniline (21) > p-nitrophenol (22.5) >
o-nitrophenol (28,5) > o-nitroaniline (29).

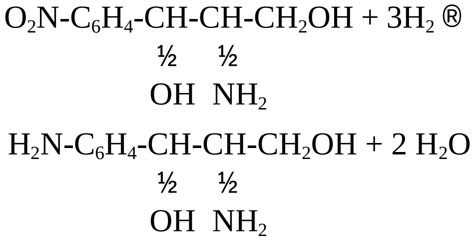
For all nitrocompounds the reaction rate decreased in following row:

ethanol > iso-propanol > THF >
benzene > water.

Such effect was connected with the polar nature of solvents and the solubility of nitrocompounds.

The optimal conditions for used nitrocompounds hydrogenation are: P = 1.0 – 4.0 MPa, T = 293-333K and as the solvent iso-propanol was selected as most suitable one.

As for 1-p-nitrophenyl-2-amino-1,3-propandiol hydrogenation it can be carried out only under heating above 343K and the optimal temperature is 363-373K.



$$\begin{array}{l} O_2N\text{-}C_6H_4\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}\underset{\substack{|\\ NH_2}}{CH}\text{-}CH_2OH + 3H_2 \rightarrow \\ H_2N\text{-}C_6H_4\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}\underset{\substack{|\\ NH_2}}{CH}\text{-}CH_2OH + 2\,H_2O \end{array}$$

The yields of 1-p-aminophenyl-2-amino-1,3-propandiol were 98-99%. The obtained product can be used as a monomer for the condensation reactions and as semiproduct for levomycetin synthesis.

2. Hydrogenation of aromatic hydrocarbons

Pd containing catalysts as mentioned above are the best for nitrogroup hydrogenation. For aromatic ring hydrogenation Rh- and Ru-catalysts are the most active [3,4]. So for hydrogenation of both nitrogroup and aromatic ring bifunctional catalysts containing Pd and Rh or Ru have to be used. Such binar catalysts were prepared by simultaneous and consequent co-impregnation with different metal : metal ratio. Catalysts prepared by simultaneous impregnation showed the better catalytic properties and were tested at hydrogenation of aromatic hydrocarbons.

In present study benzene, ethylbenzene and cumene were hydrogenated to obtain cyclohexane, ethylcyclohexane and iso-propyl-cyclohexane on Rh-Pd, Ru-Pd, Pd and Rh supported on alumina.

It was established that among them the most active and selective catalysts are Pd bimetallic catalysts supported on alumina. The reaction rate and yield of alicyclic hydrocarbons decrease by following row:

Rh-Pd > Ru-Pd > Rh > Pd

It was found that benzene was hydrogenating under hydrogen pressure approximately 3.0-3.3 MPa without heating and cumene and ethylbenzene hydrogenation needed moderate heating to 353-373K. This conditions are more mild than known from literature [7]. The reaction rate is decreasing by complication of compounds structure:

benzene >> ethylbenzene > cumene

The yields of final products for all substrates are 96-99%.

3. Hydrogenation of aromatic nitrocompounds to alicyclic amines

a) Hydrogenation of nitrobenzene

The process of aniline producing from nitrobenzene is well known [4] but nitrobenzene hydrogenation to cyclohexylamine is insufficiently studied. In industry cyclohexylamine is produced from aniline under strict conditions and used for cyclohexanone production, in rubber and cellulose-paper industry.

It was already shown that on monometallic Pd catalyst only nitrogroup was hydrogenated. The addition of the second metal to Pd leads to hydrogenation of aromatic ring too. NO_2-group and aromatic ring were consequently reduced on all used bimetallic catalysts.

By-products of nitrobenzene (NB) hydrogenation to cyclohexylamine (CHA) were dicyclohexylamine (DCHA), cyclohexanone (CHON), cyclohexanol (CHOL) - total not more than 4-5% (Table 1). The content and amount of by-products depended on the catalysts and conditions. For Rh-Pt (9:1), Rh-Pd (9:1) only DCHA was obtained.

It was established that the most active and selective catalysts for this process were Rh, Rh-Pt, Rh-Pd (Table 2). Ru-contained catalysts was the less active catalyst. On Ru catalysts both NO_2-group and aromatic ring rates were small and CHA yield wasn’t more than 70%. Thus addition of Pd and Pt to Rh resulted to higher yields and rates, but presence of Ru on the contrary decreased amounts of CHA in catalysate.

To understand the catalytic properties of tested catalysts the characterisation by some physical methods has been done. But XRD didn’t give any useful information. SEM has shown that the addition of the second metal (Rh) to Pd increased the crystallinity of the active phase as compare to pure Pd. In Pd-Ru-catalysts on the surface only Pd was observed. This may explain the low activity of these catalysts similar to pure Pd. Among the methods only TPD has given satisfactory data for interpretation of catalytic behaviour (Table 2). TPD data showed that on less active catalysts such as Rh, Pd, Rh-Ru, Ru-Pd there were two and more forms of adsorbed hydrogen with different strength of adsorption. On the contrary the best catalysts as Pt-Rh and Rh-Pd(9:1) had uniformly adsorbed hydrogen with the average strength which is probably the optimal form for our process. These data correlated with the rates (TOF) and yields of product (Table 2) and also showed metal-metal interaction in catalysts.

b) Hydrogenation of crown-ethers

Information about reduction of dinitrodibenzo-crown-ethers is very small in number. Catalytic reduction of dinitrodibenzo-crown-ethers may lead to

Table 1

Nitrobenzene hydrogenation to CHA, P=1.0 MPa, T=293 K(1-CHA, 2-DCHA, 3-CHON, 4-CHOL, 5-AN)

Catalysts	Products composition, %				
	1	2	3	4	5
Rh	90	1.0	-	2.0	7.0
Rh - Pd (9:1)	95	0.9	-	-	4.1
Rh - Pd (1:1)*	87	3.0	0.5	1.0	8.5
Rh - Pd (1:1)**	88	0.2	0.2	0.8	10.8
Rh - Pt (9:1)	98	0.7	-	-	1.3
Rh - Ru	60	0.8	1.2	-	38
Pd - Ru	62	0.5	0.5	-	37.0

*, ** - the catalysts were prepared by different methods of reduction

Table 2

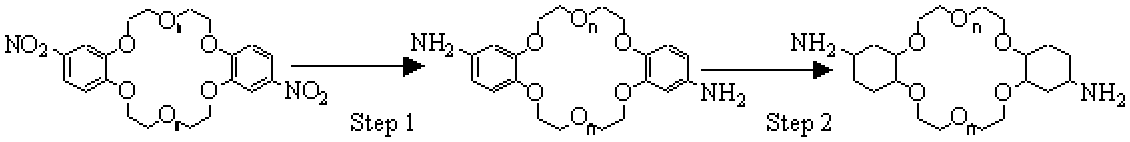
Nitrobenzene hydrogenation at P=1.0 MPa, T=293K, S - surface area,
$T_{max\ H2}$ - maximum of hydrogen thermodesorption, TOF – turnover frequency, t - process duration

Catalysts	S, m^2/g	T_{max} H_2	TOF, s^{-1}	t, min	CHA yield, %
Rh	114	441 674	0.78	190	90
Rh-Pd (9:1)	161	475 678 (small)	1.09	180	95
Rh-Pd (1:1)*	136	493 588	0.29	300	87
Rh-Pd (1:1)**	157	493 588	0.32	240.	88
Rh-Pt (9:1)	138	551	1.23	190	98
Rh-Ru	-	-	0.38	320	60
Pd-Ru	110	495 693	0.21	330	62
Pd	170	505 670	-	-	-

diaminodibenzo- and diaminodicyclohexyl-crown-ethers production. By literature data [8,9] this process was carried out in presence of large amounts of catalysts in strict conditions.

The hydrogenation of dinitrodibenzo-18-crown-6-ether (DNDB 18, 6), dinitrodibenzo-24-crown-8-ether (DNDB 24, 8) and dinitrodibenzo-30-crown-10-ether (DNDB 30, 10) to corresponding diaminodibenzo-crown ethers (DADB) and diaminodicyclohexyl-crown ethers (DADCH) by Scheme 1. These ethers are used for high selective sorbents and phase-transfer catalysts [8].

Scheme 1.



As nitrobenzene was the model substance the same best catalysts were used for crown-ethers: Pt-Rh and Rh-Pd.

The hydrogenation of only nitrogroups was carried out on monometallic Pd (the yields of DNDB are 80-92%). Hydrogenation of both nitrogroups and aromatic rings took place on bimetallic Rh-Pd and Rh-Pt catalysts.

It was determined that support nature influenced on results of reaction. On Rh-Pt/Al_2O_3 catalysts the reduction of NO_2-groups and aromatic rings were one after another (consecutive reduction), i.e. first of all DADB were formed and then, after absorbing of 6 mole of hydrogen, DADCH were formed. In contrast, on Rh-Pt/SiO_2 catalysts the reduction of NO_2-groups and aromatic rings was competitive.

It was found that the most suitable catalysts for the DADCH production were 4% and 5% Rh-Pt catalysts supported on Al_2O_3 (85-98%) and 5% Rh-Pt/SiO_2 (70-80%) (Table 3). The peculiarity of this process was to keep the oxygen crown without destruction. Oxygen crown is very sensitive to heating. By IR-analysis the absence of any change in the oxygen-crown was showed.

Conclusions

Active, selective bifunctional Rh-Pd and Rh-Pt catalysts and optimal conditions (temperature, hydrogen pressure and solvent) have been found for obtaining the alicyclic amines with high yields by hydrogenation of aromatic nitrocompounds. Such catalytic properties of these catalysts were connected with metal-metal interaction and consequently uniform state and adsorption strength of hydrogen.

References

1. M.Studer,5th Inter.Symp.Heterogen.Catal&Fine Chemicals,Lyon,(1999)KL3
2. D.R.Patel,M.K.Dalal,R.N.Ram, J.Molec. Catal.A, 109(1996)141
3. P.V.Kavantri, S.B.Chandalia, Ind.Eng.Chem. Proc.,21(1982)186.
4. S.Nishimura, Bull.Soc.Chem.Japan,34(1961)32.
5. USA patent 3678108 (1972).
6. A.D.Shebaldova, L.M.Hidekel, J.Org.Chem., 12(1976)806.
7. J.M.Orozco, O.Webb, Appl.Catal.,6(1983)67.
8. M.Hiraoka. Crown-ethers. Tokyo. Kadansha. 1982.
9. R.N.Gurski etc. 3rd Sov.Conf, on Chem& Biochem. Macrocycle Compounds, Ivanovo,1(1988)46.

Received 1 February 2000.