Amination of benzene in the presence of ammonia using a Group VIII metal supported on a carrier as catalyst

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Received 9 December 1997; accepted 17 June 1998

Benzene is selectively aminated to aniline in the presence of ammonia using a Group VIII element as the catalyst supported on a carrier at elevated temperatures and high pressures. The catalytic tests were performed in a plug flow reactor or in a continuously stirred tank reactor. To shift the reaction equilibrium towards aniline, oxygen or carbon monoxide, respectively, were added.

Keywords: aniline, benzene, heterogeneous catalysis

1. Introduction

Methods for producing aniline include the reduction of nitrobenzene with hydrogen [1] or the substitution of the phenolic hydroxyl group [2] or a halogen [3] by an amino group [4].

There are, however, also methods known for the direct amination of aromatic compounds (equation 1).

For example, in 1917 Wibaut [5] already reported on the direct amination of benzene with ammonia using a nickel/iron catalyst in the temperature range of 550–600 °C under atmospheric pressure. In 1958 a process was described that occurred at 1000 °C in the presence of a platinum catalyst, under the addition of oxygen in order to shift the reaction equilibrium [6]. Another method [7] involves a catalyst that consists of Group VI-B metal (e.g., molybdenum) together with a promoter consisting of an easily reducible metal oxide such as the oxides of copper(II), iron(III), nickel, silver or gold. DuPont developed a conditioned nickel/nickel oxide catalyst as a dehydrogenation agent [8,9]. In this case the NiO is reduced by the co-product hydrogen, converting it to its metallic form thus losing its activity. The cataloreactant may either be regenerated intermittently or continuously using oxygen or an oxygen-containing gas such as air. Finally, in 1994 Kiyo [10] presented a simultaneous selective amination (aniline) and/or cyanation (benzonitrile) process of aromatic hydrocarbons with ammonia using a Group VIII element supported on a carrier as the catalyst.

2. Experimental

2.1. Apparatus and reaction procedure

The reactions were carried out in a plug flow reactor (PFR) or in a continuously stirred tank reactor (CSTR). Benzene was mixed with ammonia in the desired ratio (1 : 15–1 : 55). The feed (WHSV = 1 h^{-1}) passed down flow through the stainless steel reactor (1.4571, 0.3 m long and 9 mm inner diameter) containing a 3 g catalyst bed. The temperature was controlled by an SPS system (ABB) and the hydrogen flow by thermal flow controllers (Brooks). Benzene and ammonia were dosed by high-pressure pumps (Latek P-402, P-700). Catalysts placed in the reactor were firstly reduced in flowing hydrogen (500 °C, 2 h) and the temperature was lowered to the reaction temperature. The products were analysed with an on-line gas chromatograph (Carlo Erba 2100; 3 m × 3.1 mm column Cromosorb 103, isotherm 220 °C). Products were identified using mass spectroscopy.

A continuously stirred tank reactor (CSTR) was used to determine the influence of the reactor type. In comparison to the PFR (integral reactor), the Carberry reactor [11] (differential reactor) is clearly superior in that various transport gradients are minimized.

2.2. Materials

Hydrogen (5.0 Westfalengas AG) and ammonia (BASF AG) were used without further purification. Purity of the reactant quoted by the manufacturer: benzene (Fluka AG) p.a. >99.5%.

2.3. Preparation of catalysts

All the catalysts had a loading of 0.5 wt% noble metal/carrier. The carriers used were alumina, silica and zeolites (e.g., NaX, H-ZSM-5, H-β). The Group VIII element was brought on the carriers by wet impregnation (e.g., for alumina, silica), by ion exchange (e.g., zeolites) or by a special sol–gel method. All the platinium group metal/alumina catalysts (e.g., Ru, Rh, Pd, Pt/Al_2O_3) used in this study were prepared by a special sol–gel method [12]

Table 1
Oil-drop catalysts.

Metal	Cat. no.	d_P(BJH) (nm)	S_{BET} ($m^2\,g^{-1}$)
0.5% Pd	JBK 3	6.1	244
0.5% Pt	JBK 21	6.0	232
0.5% Ru	JBK 26	4.3	300
0.5% Rh	JBK 29	5.4	228

(table 1). The samples were calcined in air (550 °C, 6 h) and finally reduced in flowing hydrogen (500 °C, 2 h).

3. Results and discussion

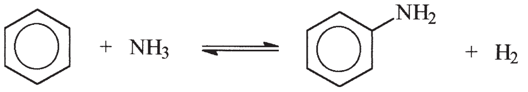
3.1. Thermodynamics

The thermodynamic data for the gas phase reactions (equations 1–5) in the temperature range 25–600 °C were determined with the method of van Krevelen and Chermin [13] and shown in figure 1. The maximum aniline yields (1) which can be expected as a function of temperature and the molar ratio are presented in figure 2.

The free reaction enthalpy ΔG_R of the amination of benzene is in the considered temperature range larger than zero. For the ammonia decomposition, which can run down parallel to the aniline formation, the free reaction enthalpy is negative for temperatures higher than 200 °C and is increasing with decreasing temperature. The aniline formation can be influenced by the favoured ammonia decomposition.

Figure 2 shows the attainable turnover as a function of the temperature and the ammonia/benzene molar ratio.

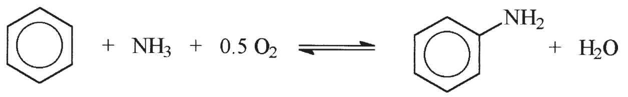
The reaction enthalpy ΔH_R of the amination of benzene is positive in the considered temperature range.



Equation 1.

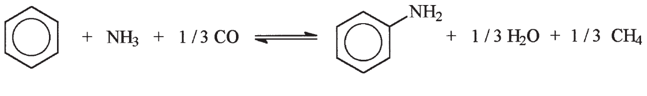
$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2$$

Equation 2.



Equation 3.

Equation 4.



Equation 5.

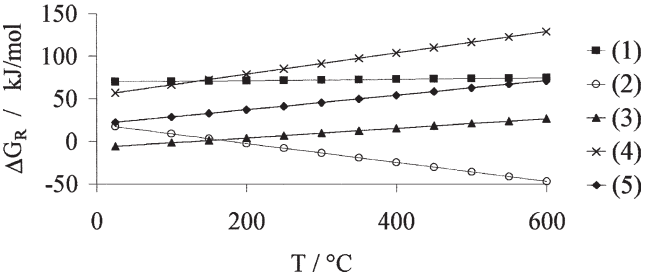


Figure 1. Free reaction enthalpy of the amination of benzene (1), amination of benzene in presence of oxygen (3), amination of benzene in presence of carbon monoxide (4,5) and the decomposition of ammonia (2) dependent on temperature.

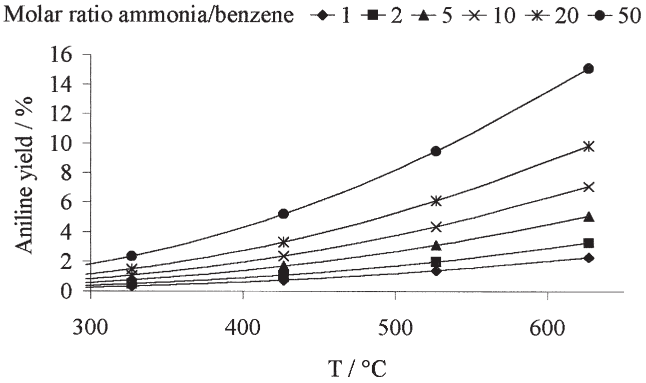


Figure 2. Theoretical maximum aniline yield as a function of temperature and the molar ratio.

The thermodynamic data in figure 1 shows that the presence of oxygen (3) and carbon monoxide (4,5) should influence the reaction equilibrium.

3.2. Influence of the reaction pressure

The transformation under atmospheric pressure shows only a low selectivity to aniline. Methane, toluene and benzonitrile are obtained almost exclusively as by-product as mentioned also in [10]. Table 2 shows that by increasing the reaction pressure to more than 30 bar the by-product formation can be driven back. An exact explanation cannot be given presently. Aniline (up to 2%) and methane can be obtained as the only products.

3.3. Influence of the temperature

The thermodynamic data (figure 2) show that the aniline equilibrium turnover increases with rising temperature.

Table 2
Amination of benzene dependent upon pressure (0.5% Pd/NaX-zeolite, $C_6H_6 : NH_3 = 1:55$, $T = 500\,°C$, TOS = 4 h).

p	Conv. PhH	Selectivity (%)		
(bar)	(%)	$PhCH_3$	$PhNH_2$	PhCN
1.4	1.90	48	24	27
2.5	1.84	61	30	8
4.0	1.81	25	62	12
30	0.98	0	99	0

Table 3
Amination of benzene dependent on temperature ($C_6H_6 : NH_3 = 1:55$, $p = 50$ bar).

Catalyst	T (°C)	TOS (h)	Yield aniline (%)
0.5% Ru/Al_2O_3	400	3	0.82
0.5% Ru/Al_2O_3	450	3	1.21
0.5% Ru/Al_2O_3	500	3	0.60
0.5% Ru/Al_2O_3	550	3	0.35

Table 4
Amination of benzene using different catalysts (0.5% metal/Al_2O_3, $C_6H_6 : NH_3 = 1:55$, $p = 50$ bar).

Catalyst	T (°C)	TOS (h)	Conv. benzene (%)	Select. aniline (%)
Ru/Al_2O_3	450	9	1.21	99
Rh/Al_2O_3	500	6.5	1.40	99
Pd/Al_2O_3	500	5	1.42	88
Pt/Al_2O_3	500	3.5	1.26	92

The aniline yield is the highest at 450 °C (table 3); at lower and higher temperatures the yield is much lower. This is probably due to the increasing ammonia decomposition (equation 2) at higher temperatures; the hydrogen leads to a hydrodenitrogenation [14], thus decreasing the aniline yield. The formation of benzene by hydrodenitrogenation of aniline is thermodynamically possible, except for temperatures >400 °C, as shown by Schulz et al. [14]. The aniline yield is reduced by the addition of hydrogen and is independent of both pressure and temperature.

3.4. Amination using different noble metals

In table 4 the results of the amination in the presence of different noble metals loaded catalysts are presented. There is not an extreme difference between the various Group VIII metals.

3.5. Influence of the reduction conditions

The catalysts were firstly reduced in flowing hydrogen (500 °C, 2 h). In figure 3 the aniline yield is depicted for a reduction with a heating rate of 10 °C min^{-1} to 500 °C and in figure 4 with 0.5 °C min^{-1} to 500 °C.

The results show that the lifetime of the catalysts can be increased through a heating rate of 0.5 °C min^{-1} during the reduction.

3.6. Using a Carberry reactor

The deployment of a CSTR (2 g catalyst; Ru, Rh, Pd, Pr/Al_2O_3; $C_6H_6 : NH_3 = 1:55$; $T = 500$ °C; $p = 50$ bar) does not result in a production of aniline. Using this system an increase in ammonia decomposition (2) can be observed; aniline production did not occur.

One of the limiting factors of the direct amination is the formation of hydrogen. The reaction time is too long and a long residence time favours the decomposition of ammonia. The formed hydrogen shifts the equilibrium of the direct amination to the side of benzene.

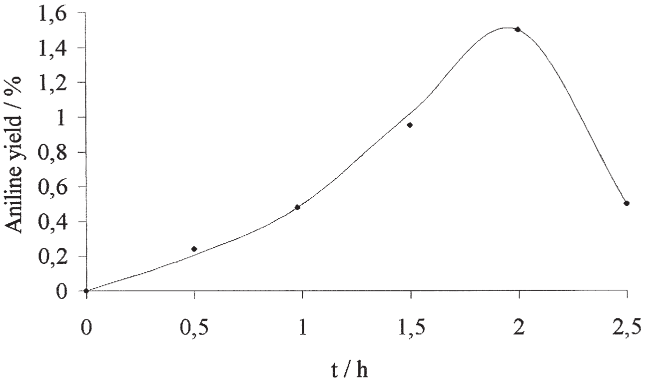


Figure 3. Amination of benzene dependent on reaction time, 2 g (0.5% Pd, 0.5% Cs, Al_2O_3), $C_6H_6 : NH_3 = 1:55$, $p = 50$ bar, $T = 500$ °C, WHSV = 1.6 h^{-1}, reduction (H_2, 2 h, 500 °C, 10 °C min^{-1}).

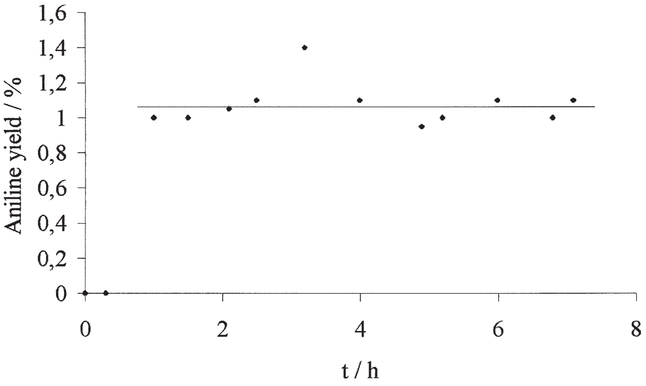


Figure 4. Amination of benzene dependent on reaction time, 2 g (0.5% Pd, 0.5% Cs, Al_2O_3), $C_6H_6 : NH_3 = 1:55$, $p = 50$ bar, $T = 500$ °C, WHSV = 1.6 h^{-1}, reduction (H_2, 2 h, 500 °C, 0.5 °C min^{-1}).

3.7. Amination in presence of addition materials

The amination of benzene leads only to slight turnovers and yields. In order to shift the reaction, equilibrium oxygen (equation 3) or carbon monoxide (equations 4, 5) was added as an oxidant.

Oxygen. The amination process was carried out both batchwise (b) and in a continuous operation (c). The batchwise catalytic results in table 5 show that the amination in the presence of air only led to minor aniline yields. Ani-

Table 5
Amination of benzene in presence of oxygen ($C_6H_6 : NH_3 : O_2 = 1:55:1$–5).

	Catalyst	T (°C)	p (bar)	Conv. benzene (%)	Select. aniline (%)
b	2% Pd/Al_2O_3	250	260	1.1	9
c	36% Ni/Al_2O_3	400	1	1.5	87
c	46% Ni/Al_2O_3	400	50	1.6	80
c	CuO/ZnO	450	50	1.5	87

Table 6
Amination of benzene in presence of carbon monoxide ($C_6H_6 : NH_3 : CO = 1:55:1$).

Catalyst	T (°C)	p (bar)	Conv. benzene (%)	Select. aniline (%)
30% Ni/SiO_2	475	50	6.0	33
43% Ni/Al_2O_3	400	50	3.0	50
46% Ni/Al_2O_3	450	50	2.0	40
CuO/ZnO	450	12	3.0	34

line, benzonitrile, phenol and nitrobenzene were obtained in small amounts. The reaction temperature of the gas phase amination can be reduced slightly from 450 to 400 °C by the application of air.

Carbon monoxide. In table 6 the results of the amination in the presence of carbon monoxide are presented. Carbon monoxide had no influence on the aniline yield, the selectivity is much lower.

4. Conclusions

In summary, we have developed a method for the catalytic direct amination of aniline from benzene at an elevated temperature and under high pressure. By increasing the pressure to 50 bar the by-product formation of toluene and benzonitrile can be reduced. A limiting factor of the direct amination is the formation of hydrogen due to an increasing ammonia decomposition at higher temperatures.

Acknowledgement

The financial support of Hoechst AG is gratefully acknowledged. We would like to thank Professor Dr. K. Kühlein and Dr. U. Dingerdissen for their interest in this work and the authorization for publication.

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