Catalysis Letters Vol. 103, Nos. 1–2, September 2005 (© 2005)
DOI: 10.1007/s10562-005-6525-3

On the mechanism of the oxidative amination of benzene with ammonia to aniline over NiO/ZrO_2 as cataloreactant

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Received 19 April 2005; accepted 20 May 2005

The kinetics of the semi-batch oxidative synthesis of aniline under atmospheric pressure using DuPont's NiO/ZrO_2 cataloreactant was studied in a microreactor flow set-up equipped with a calibrated online mass spectrometer. It was found that the reaction temperature is a crucial parameter for the selectivity to aniline. At 590 K, exclusively aniline was formed, whereas at higher temperatures the decomposition of benzene into C-1 fragments led to the formation of toluene and benzonitrile. TPO experiments carried out in the same reactor subsequent to isothermal aniline synthesis allowed us to derive the degree of coking and the degree of NiO reduction.

KEY WORDS: aniline; benzene; direct amination; nickel oxide; cataloreactant.

1. Introduction

The large-scale production of aniline is based on several routes including the reduction of nitrobenzene and the reaction of chlorobenzene or phenol with ammonia [1–4]. A very attractive path for the synthesis of aniline is the direct amination of benzene. Already in 1917 Wibaut [5] reported the direct synthesis of aniline by passing benzene and ammonia over a iron/nickel catalyst in the temperature range from 550 to 600 °C. Numerous approaches were tried to enhance the yield of aniline by overcoming the thermodynamic equilibrium limitation of this process, mostly by converting the coupled product hydrogen with oxygen to water. Oxygen was added either as molecular species [6–11] or as lattice-bound anions using a reducible metal oxide [8,12]. In the latter case, the reducible oxide is called a cataloreactant which acts as a catalyst as well as a reactant. But none of the mentioned direct routes was ever used commercially because of the low degree of C_6H_6 conversion and/or the low aniline selectivity. DuPont developed the up to now most successful cataloreactant containing NiO/ZrO_2 [13–16]:

Although DuPont's cataloreactant achieved relatively high aniline yields amounting to 13.6% at 623 K and 300–400 atm, this process was not commercialized either.

In a combinatorial approach by Hagemeyer *et al.* [17], about 25,000 samples were tested in batch reactors, leading to the result that NiO is indeed the most active oxidant and that ZrO_2 and K_xTiO_2 are the most suitable carriers. To improve the DuPont system, the authors suggest the addition of a noble metal such as Rh and a dopant such as Mn to stabilize NiO [17]: the noble metal should act as catalyst instead of Ni metal thus saving an additional reducing pretreatment, and the Mn dopant should improve the regenerability.

However, according to the knowledge-based approach, information on the reaction mechanism must be gained first to provide a firm starting point for improving the catalyst. Furthermore, continuous oxidative aniline synthesis under lower pressures is advantageous for a commercially viable process regarding costs and regeneration of the cataloreactant. For these reasons, we established semi-batch oxidative aniline synthesis under atmospheric pressure using DuPont's cataloreactant. For the first time, information on the reaction network and on the state of the cataloreactant was derived from isothermal and temperature-programmed kinetic experiments using a calibrated online mass spectrometer.

2. Experimental

All experiments were carried out at ambient pressure in a stainless steel microreactor set-up equipped with a saturator filled with C_6H_6 (Sigma-Aldrich, 99.9%) and gas lines for Ar (purity 99.9999%), 8% NH_3 in He, and 1% O_2 in He (Messer Griesheim). The gas flows were adjusted by mass flow controllers (Brooks). The concentration of benzene was established by the temperature of the saturator (283 K). Online gas analysis was performed by a quadrupole mass spectrometer (Balzers, Omnistar) which was calibrated for N_2, H_2, NH_3, H_2O, CO_2, benzene, aniline, toluene, and benzonitrile. The experiments were carried out with a NiO/ZrO_2 catalyst

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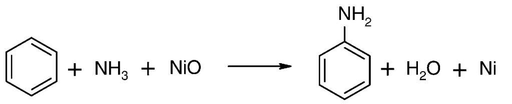
1011-372X/05/0900–0155/0

(approx. 40 wt% NiO) prepared by coprecipitation as described in Ref. [13]. In this study, 100 mg of the 250–355 μm sieve fraction were filled into the reactor consisting of a glass-lined U-tube with an inner diameter of 4 mm resulting in a bed height of about 12 mm. The temperature was measured directly above the catalyst bed using a thermocouple.

The isothermal aniline synthesis experiments were carried out at 590, 620, and 670 K using a fresh catalore-actant sample for each experiment. Prior to aniline synthesis, the catalyst was pretreated at 383 K for 1 h to remove weakly chemisorbed H_2O in flowing Ar (60 Nml min^{-1}). Then, the catalyst was heated to the chosen reaction temperature using a ramp of 6 K min^{-1}. The subsequent isothermal aniline synthesis experiment was carried out using a gas mixture containing 0.5% C_6H_6 and 5% NH_3 in inert gas at a total flow rate of 150 N ml min^{-1}.

After each synthesis experiment the catalyst was cooled to room temperature in flowing Ar, and a temperature-programmed oxidation (TPO) experiment was performed in the same set-up by exposing the catalyst to a mixture of 1% O_2 in He at a flow rate of 70 N ml min^{-1}. The temperature was first increased up to 623 K with a heating ramp of 15 K min^{-1}, and then held for 60 min at this temperature. Based on the consumption of O_2 and the formation of H_2O and CO_2, the degree of reduction of NiO was derived. Oxygen which was consumed for burning off coke deposits (equation (2)) was subtracted from the total consumption of oxygen:



(1)

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \qquad (2)$$

The residual amount of the oxygen consumption was then correlated with the re-oxidation of Ni^0(equation (3)) which had been formed during aniline synthesis:

$$2Ni + O_2 \rightarrow 2NiO \qquad (3)$$

Finally, the reduction degree of NiO (X(NiO)) was calculated according to equation (4), where $n(O_2)$ is the consumed amount of oxygen, $n(H_2O)$ and $n(CO_2)$ are the formed amounts of H_2O and CO_2, respectively, and $n_0(NiO)$ is the amount of NiO which was applied for the isothermal aniline experiments:

$$X(NiO) = \frac{\left(n(O_2) - n(CO_2) - \frac{1}{2} \cdot n(H_2O)\right) \cdot 2}{n_0(NiO)} \qquad (4)$$

3. Results and discussion

In literature, side reactions such as deep oxidation of C_6H_6 [11], coking [18] and the formation of benzonitrile and toluene [19] are reported. Therefore, the concentrations of NH_3, C_6H_6, H_2O, aniline, and the concentrations of the possible byproducts CO_2, N_2, H_2, toluene

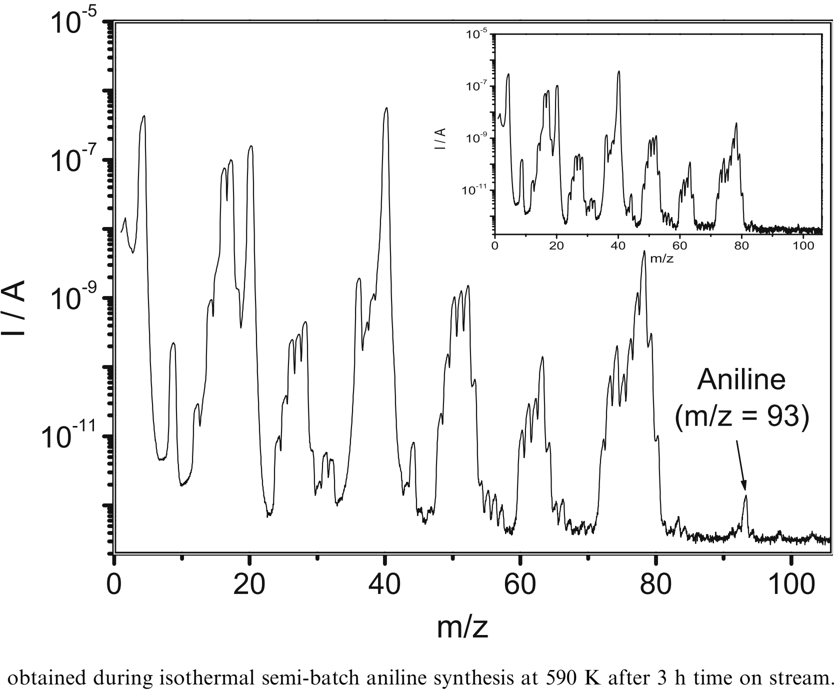
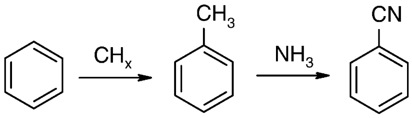


Figure 1. Mass spectrum obtained during isothermal semi-batch aniline synthesis at 590 K after 3 h time on stream. The inset shows the mass spectrum of the reactant mixture obtained before the reactor was switched online.

and benzonitrile were measured in this study by means of a calibrated online mass spectrometer. Simultaneously, the ion currents of the following masses were monitored in order to test for further plausible byproducts: m/z = 84 (cyclohexane), 94, 95 (phenol), 106, 107 (toluidines, xylenes) and 117 (tolunitriles). In addition to the measurement of the concentrations and the ion currents, a mass spectrum was recorded after a time on stream (TOS) of 3 h. Figure 1 shows the mass spectrum obtained for the isothermal aniline synthesis at 590 K. The striking observation is the peak at $m/z = 93$ which can be reliably assigned to the M^+ ion of aniline formed according to equation (1). Its intensity yields a concentration of about 2 ppm.

Furthermore, no other peaks which would indicate the formation of other aromatic byproducts and of cyclohexane were found. For comparison, the mass spectrum of the reactant mixture obtained before the reactor was switched online is shown in the inset of figure 1. There is no significant difference between the mass spectrum of the reactant mixture and the mass spectrum obtained after a TOS of 3 h except for the peaks of aniline. Thus, the mass spectrum indicates that at 590 K side reactions such as the decomposition of NH_3 and the deep oxidation of C_6H_6 did not occur to a significant extent.

Aniline synthesis was also carried out at 620 K which is the reaction temperature applied by DuPont for the batch experiments [13–16]. Under the chosen reaction conditions an equilibrium conversion of C_6H_6 of 4% was calculated for the reaction of C_6H_6 and NH_3 forming H_2 and aniline. Figure 2 shows the concentration profiles of the products obtained for aniline synthesis at 620 K. The recorded mass spectrum and the measured ion currents provide no evidence for the presence of other aromatic compounds than aniline and benzonitrile. The occurrence of N_2 indicates the decomposition of NH_3, whereas produced CO_2 points to the deep oxidation of C_6H_6. H_2 originates both from the decomposition of NH_3 and of C_6H_6. The onset of the decline in aniline concentration and the onset of the deep oxidation of C_6H_6 took place simultaneously followed by a further increase in the benzonitrile concentration suggesting that high temperatures favor the formation of benzonitrile instead of the formation of aniline as a consequence of deep oxidation yielding C-1 fragments:



(5)

In order to check this conjecture, aniline synthesis was performed at an even higher reaction temperature of 670 K under otherwise identical experimental conditions. Deep oxidation of C_6H_6 to CO_2 and H_2O was observed right at the beginning of the reaction as shown in figure 3. The yield of aniline was rather low, whereas the yield of benzonitrile was higher compared with the two previous experiments. The temporal course of the concentration of toluene suggests that the formation of benzonitrile proceeds sequentially via toluene (equation (5)). No evidence for the presence of cyclohexane and the other aromatic hydrocarbons mentioned above was found.

In the course of the reaction at 670 K the formation of CO_2 and H_2O stopped indicating the complete reduction of NiO. This observation agrees with the result of the subsequently performed TPO experiment described in the following. From a mechanistic point of view, the decomposition of C_6H_6 into C-1 fragments which obviously also takes place in the absence of oxygen is necessary for the ongoing formation of the byproducts toluene and benzonitrile. Furthermore, our data show that even after the full reduction of NiO into Ni^0, the formation of aniline is still possible with low selectivity in agreement with the pioneering work by Wibaut [5].

Subsequent to aniline synthesis, TPO experiments were carried out to determine the degree of conversion of NiO. Figure 4 displays the TPO profiles obtained subsequent to aniline synthesis at 620 K. The CO_2 peak demonstrates that coking had taken place during aniline synthesis. Since a H_2O peak was also observed, obviously hydrogen-containing carbonaceous species had been deposited on the surface. The consumption of oxygen began immediately, when the heating ramp

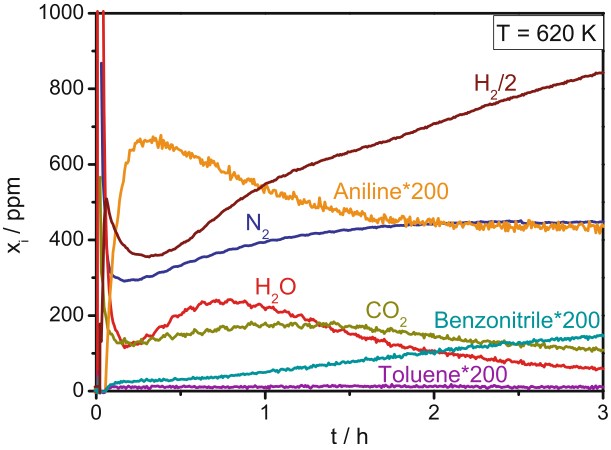


Figure 2. Concentration profiles of the products obtained for the isothermal semi-batch aniline synthesis at 620 K.

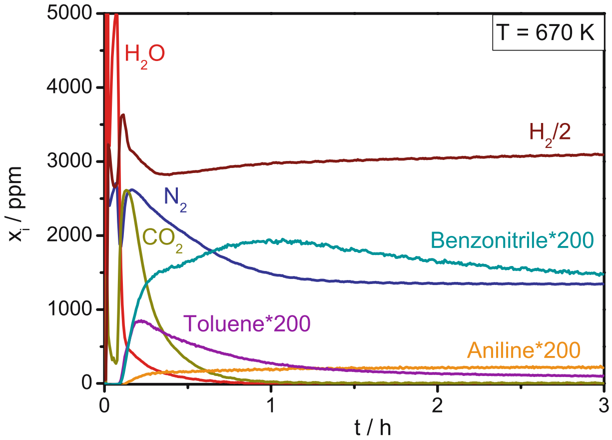


Figure 3. Concentration profiles of the products obtained for the isothermal semi-batch aniline synthesis at 670 K.

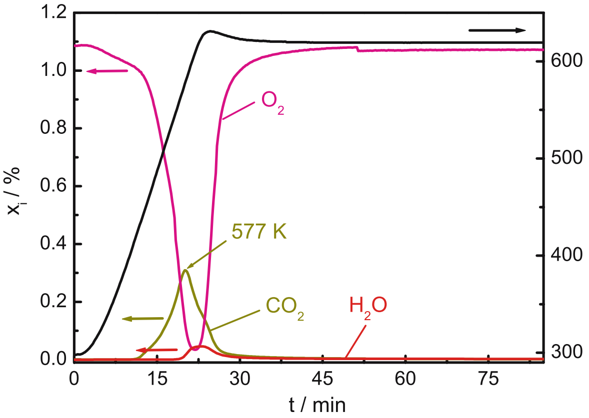


Figure 4. TPO profiles obtained subsequent to aniline synthesis at 620 K.

Table 1
NiO conversion and degree of coking after 3 h aniline synthesis

Temperature of aniline synthesis (K)		590	620	670
NiO conversion (%)		30	60	110
Amount (μmol)	CO_2	20	70	110
	H_2O	10	10	0

started at room temperature, whereas the formation of CO_2 did not start before a temperature of 410 K was reached. The oxygen consumption which occurred prior to the onset of CO_2 formation can be attributed to the re-oxidation of Ni^0 formed under the reducing aniline synthesis conditions. This hypothesis is supported by the observation of a sudden oxidation of about 80% of previously hydrogen-reduced Ni^0 at room temperature, when the reactor was switched online. Obviously, the carbon deposits on the surface render the oxidation of Ni^0 more difficult, but a slight oxidation before the start of the temperature program cannot be ruled out.

The determined degrees of NiO conversion are summarized in table 1. The NiO conversion increased up to 100% with increasing reaction temperature of aniline synthesis. Since the formation of nitric oxides and CO was neglected, too high degrees of conversion were found for the synthesis at 670 K. CO can be formed in addition to CO_2 when burning off the coke deposits, and the reaction of molecular oxygen with residual adsorbed NH_x species can lead to the formation of nitric oxides. In summary, the TPO results show that coking took place during aniline synthesis at 590, 620, and 670 K, and that the degree of coking increased with rising synthesis temperature. At the highest temperature, carbonaceous species containing very little hydrogen were deposited on the surface.

4. Conclusions

Our results show that semi-batch oxidative aniline synthesis is possible at atmospheric pressure using supported NiO as cataloreactant. It was found that the reaction temperature is a crucial parameter for the selectivity to aniline. At temperatures below 610 K, aniline was detected as the only aromatic product. At higher temperatures, the decomposition of benzene into C-1 fragments leads also to the formation of benzonitrile, presumably via toluene as reaction intermediate. Other aromatic products were not observed. Subsequently performed TPO experiments are a useful tool to derive the degree of coking and the degree of reduction of NiO during aniline synthesis.

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