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Hydrodenitrogenation of Aniline over Ni–W/Al_2O_3 Catalyst

Aromatic amines, such as aniline, are present not only in crude oils but also and more importantly in the intermediate products in the hydrotreatment of nitrogen-containing heterocyclic compounds (*1–4*). However, these amines have not been extensively studied under the conditions of hydrodenitrogenation (HDN).

The HDN reaction has been investigated with various nitrogen-containing compounds such as aliphatic amines (pentylamine) (*5–7*), cyclic amines (piperidine) (*8–11*), basic heterocycles (pyridine, quinoline) (*9, 11–18*), and non-basic heterocycles such as pyrrole, indole, or carbazole (*17–20*). Some work has been carried out concerning the hydrodenitrogenation of aniline. For instance, on metallic Ni deposited on clays the production of *N*-phenylcyclohexylamine from aniline was studied (*21*). By contrast, on Co catalysts, depending on the conditions, there is the formation of cyclohexylamine, dicyclohexylamine, and cyclohexane (*22*). Also, on a variety of Ni–Mo–W/Al_2O_3 catalysts the predominant reaction is the hydrogenation of the aromatic ring with very little hydrogenolysis of the C_{sp^2}–N bond, forming benzene (*23*). In reactions taking place on Ni–Co–Mo, Co–Mo, Ni–Mo, and Ni–W catalysts (*24*), benzene is found to predominate in the reaction products, thus suggesting that C_{sp^2}–N bond scission is the main route and aniline does not necessarily have to be transformed to cyclohexylamine in order to be denitrogenated.

These results show that the studies of the reaction scheme of the HDN of aniline present only preliminary and sometimes contradictory conclusions. The objective of the experiments described here was to study this HDN reaction and to clarify the process of elimination of nitrogen at 250–390°C and P_{H_2} = 6 MPa, on presulfided Ni–W catalyst.

The experiments were carried out in a 0.3-liter stirred autoclave (Autoclave Engineers type Magnedrive), operating in a batch mode, with a system for sampling of liquid during the course of the reaction. The Ni–W catalyst used was Procatalyst HR 354 which has the composition 3% NiO, 23% WO_3, and 74% Al_2O_3. It was sulfided following a previously described method (*25*).

The reactants used were commercial products, the solvent was n-decane, and the internal standard for gas chromatographic (GC) analyses was *n*-hexadecane. Analyses were performed on a Girdel 3000 gas chromatograph equipped with a flame ionization detector and using nitrogen as carrier gas. Two types of column were used: (i) OV 17 Pyrex column (3 m) (separation conditions: 5 min at 30°C, increase of 10°C/min to 260°C; gas flow rate: 10 cm^3/min at 70°C; injector: 300°C; detector: 300°C; (ii) SE 52 Pyrex column (3 m) (temperature from 50 to 260°C at 10°C/min, other conditions unchanged) (this column allowed an improved separation of the cyclohexylamine/*n*-decane peaks but was poor in separating aniline and the solvent).

The HDN of aniline was studied at temperatures between 250 and 390°C and under hydrogen pressure from 3 to 6 MPa. By varying the stirrer rotation speed we verified that diffusion is not a limiting step in the reaction; the rotation speed had no significant effect on the disappearance of aniline or the nature of the products formed.

The products formed during the reaction at P_{H_2} = 6 MPa were cyclohexane **4**, cyclohexene **5**, benzene **6**, and *N*-phenylcyclo-

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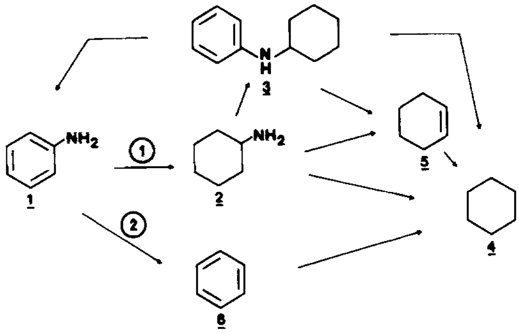

FIG. 1. Reaction scheme for hydrodenitrogenation of aniline.

hexylamine **3** (see Fig. 1 for numerical designation of compounds). Cyclohexane was the major product at reaction temperatures between 300 and 350°C. Cyclohexene was present at temperatures below 350°C and benzene at temperatures above 300°C. At 250°C the secondary amine **3** became the predominant product with cyclohexane; at higher temperatures **3** is only present in very small amounts. It is also interesting to note that at this temperature (250°C), only 10% **1** had reacted after 10 h of reaction.

The HDN of aniline was achieved by studying the effect of temperature in the range 300–390°C at $P_{H_2} = 6$ MPa (Table 1) and the determined value of the apparent activation energy for disappearance of aniline was 92 kJ mol^{-1}.

The hydrogen pressure affected the results and the rate of reaction of the HDN of aniline. Increasing the pressure up to $P_{H_2} = 5$ MPa favors the overall disappearance of aniline. Furthermore we observed a decrease in the concentration of *N*-phenylcyclohexylamine with a drop in pressure (at 1.8 MPa, this secondary amine is absent in the reaction medium) eventually due to an equilibrium $\mathbf{1} + \mathbf{5} \rightleftarrows \mathbf{3}$. The reaction order in hydrogen is close to zero at high pressures ($P_{H_2} > 6$ MPa) whereas at $P_{H_2} < 5$ MPa the reaction order in hydrogen is unity.

In benzene hydrogenation under identical conditions, ($P_{H_2} = 6$ MPa; $T = 350$°C), cyclohexane is the only product obtained. The rate of disappearance of benzene follows a first-order law. The rate constant $k_{\phi} = 24 \times 10^{-4}$ min^{-1} g cat^{-1} is one-eighth of the rate of disappearance of aniline under the same conditions.

The *N*-phenylcyclohexylamine **3** is a secondary product often encountered during the hydrogenation of aniline (*26–28*). Analyses of samples taken during the course of the hydrotreatment of **3** and the final mixture showed that hydrogenolysis of the C_{sp^3}–N bond is the first step in the formation of aniline, cyclohexene, and cyclohexane (*25*).

The hydrogenolysis of cyclohexylamine was studied under conditions ($P_{H_2} = 6$ MPa; $T = 250$ and 300°C) identical to those of the first reactions in the HDN of aniline. The saturated amine **2** rapidly undergoes self-alkylation at 250°C into dicyclohexylamine **7** (*22, 26, 29*). Twenty-five percent of **2** was transformed by simply heating in the presence of the catalyst; all of **2** disappeared after approximately 5 min of reaction. Besides the secondary saturated amine **7**, small amounts of cyclohexane **4** and cyclohexene **5** were observed. It is possible that **5** is the product of a Hoffman-type β-elimination reaction of **2** or **7** taking place at the catalytic sites (*2*). At 300°C the cyclohexylamine reacts quickly, the main product being the saturated hydrocarbon **4** with small amounts of compound **5** also being produced. The secondary amine **7** is only present in very small amounts.

TABLE 1

The Temperature Influence on the Rate Constant of Disappearance of Aniline ($P_{H_2} = 6$ MPa; catalyst: Ni–W)

Temperature (°C)	$k_{disapp} \times 10^4$ (min^{-1} g cat^{-1})
300	45
350	200
390	630

TABLE 2

Effect of Temperature on the Ratio Hydrogenation/Hydrogenolysis (i.e., Path 1/Path 2) in Aniline HDN (P_{H_2} = 6 MPa)

Temperature (°C)	$r = \frac{\text{path 1}}{\text{path 2}} = \frac{\text{hydrogenation}}{\text{hydrogenolysis}}$
300	∞
350	17–20
390	8–9

The treatment of dicyclohexylamine, under identical conditions (300°C; P_{H_2} = 6 MPa), results in the complete disappearance of the reactant after 3 h of reaction. This amine **7** produces cyclohexene, cyclohexane, and small amounts of cyclohexylamine.

Thus hydrogenation of aniline in the presence of a hydrotreating catalyst is a complex reaction. The accepted hypothesis is that this reaction which produces *N*-phenylcyclohexylamine, cyclohexene, and cyclohexane proceeds via the intermediates cyclohexylamine and benzene.

The path involving saturated amine **2** (path 1) could be the predominant path (Fig. 1). There is a little hydrogenolysis of the C_{sp^2}–N bond of **1**. This reaction occurs only at temperatures above 300°C and would be a side reaction.

The reaction of formation of amine **3** is not important in the hydrotreatment; its concentration remains consistently low in the reaction mixture.

This hypothesis of the reaction mechanism is confirmed by the study of the hydrogenolysis of the cyclohexylamine and by comparing the rate of HDN of aniline and the rate of hydrogenation of benzene at various temperatures.

The difference in the rates of disappearance of amines **2** and **7** (rate disapp. **2** $\gg$ rate disapp. **7**) and the small amount of dicyclohexylamine observed during the HDN of cyclohexylamine show that the autoalkylation of saturated amine **2** is not the only or even the predominant reaction path. At temperatures above 300°C, the hydrogenolysis of the C_{sp^3}–N bond and Hoffman-type β-elimination can be seen as the principal paths in the hydrotreatment of cyclohexylamine. Winans (*22*) proposed a similar hypothesis that the saturated amine **2** is converted directly to product **4** at temperatures above 325°C.

The rate of reaction of cyclohexylamine is much greater than that of aniline. In the HDN of **1**, saturated amine **2** is not observed, as it reacts as quickly as it is formed.

The difference between the rate of hydrogenation of benzene, k_ϕ, and the rate of conversion of aniline, k_A, ($k_\phi < k_A$) shows that the path involving aromatic hydrocarbon **6** is not the predominant path in the hydrotreatment of aniline. If it was the predominant path there would be an accumulation of benzene, which has not been observed in the reaction medium. Also the presence of aniline in the reaction mixture would inhibit the hydrogenation of compound **6** (*26*) and the difference of values k_A and k_ϕ might be more accentuated under the conditions of HDN of amine **1**.

In the general reaction scheme of the HDN of aniline (Fig. 1), process 2 (hydrogenolysis of the C_{sp^2}–N bond) becomes slightly more important with an increase in temperature, although even at 390°C 90% of the aniline is consumed by path 1 (Table 2).

This study of the hydrotreatment of aniline on a Ni–W presulfided catalyst has confirmed the complexity of the reaction mechanism which is extremely dependent on the conditions of temperature and hydrogen pressure. The essential pathway of this reaction is the saturation of the aromatic ring followed by the hydrogenolysis of the C–N bond of the saturated compound.

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