Hydrodenitrogenation of Simple Aromatic Amines on Molybdena Catalysts

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ABSTRACT

The hydrotreatment of some aromatic amines was studied at temperatures ranging from 400 to 450°C and $P_{H_2} = 1$ atm under flow conditions. Hydrogenolysis of aromatic amines involves direct cleavage of the $C(sp^2)$–N bond without saturation of the aromatic ring. The presence of hydrogen sulphide in the reaction stream has a promotional effect on the hydrogenolysis of $C(sp^3)$–N bond and an inhibitive effect on the hydrogenolysis of $C(sp^2)$–N bond. The use of a saturated hydrocarbon as diluent facilitates C–N bond hydrogenolysis in the presence of hydrogen, irrespective of the carbon being sp^2 or sp^3 hybridized.

INTRODUCTION

Hydrodenitrogenation is an important process for lowering the nitrogen content of low-grade petroleum feedstocks as nitrogen-containing compounds poison the acid catalysts used in petroleum refining. Removal of nitrogen from heterocyclic compounds is considered to take place through a two-step process: first the aromatic ring is saturated, followed by removal of nitrogen through C–N bond cleavage. It is well established that hydrodenitrogenation of aromatic nitrogen-containing heterocyclic compounds requires catalysts with a high hydrogenation activity [1–4]. Generally, these reactions are carried out at 300–1500 p.s.i.g. hydrogen and 290–450°C [5–7].

Most of the work reported in the literature has been carried out with a view to finding new catalysts or improving the yield of reactions using model compounds often diluted with hydrocarbons. Selectivity for the cleavage of C–N bonds of different types and the effect of structural variations of the amine on the selectivity have not been reported. The role of diluent hydrocarbons as hydrogen donors also has not been fully investigated. This paper reports a study of the reactions of N-methylaniline over molybdena catalysts with and without cobalt and nickel promoters, in the vapour phase, with cyclohexane and hydrogen. N-Methylaniline has both $C(sp^2)$–N and $C(sp^3)$–N bonds and

offers the possibility of investigating whether the hybridization of the carbon linked to nitrogen is a factor in a catalyst's ability to cleave the C–N bond.

EXPERIMENTAL

Amines were purified by distillation under reduced pressure and cyclohexane was purified by distillation after drying over calcium chloride. Molybdena/γ-alumina (12.4 : 87.6) was prepared by the impregnation of alumina, prepared by the solid–solid interaction method [8], with an aqueous solution of ammonium paramolybdate. It was then dried overnight at 100°C and calcined at 500°C for 6 h. For the preparation of cobalt- and nickel-promoted catalysts, γ-alumina was first impregnated with ammonium paramolybdate solution, dried overnight at 100°C and calcined at 500°C for 6 h. Nickel or cobalt was then introduced by a second impregnation with nitrate solution followed by drying and a final calcination at 500°C for 6 h. The surface area of the catalysts was determined by the BET method (Table 1).

Reduction of the catalyst was carried out at 400°C for 2 h in hydrogen flowing at a rate of 50 cm^3/min. This catalyst is referred to in this paper as MoO$_3$/Al$_2$O$_3$ (red.). Sulphidation was carried out at 400°C with hydrogen–hydrogen sulphide (9:1, v/v) flowing at a rate of 50 cm^3/min for 3 h. This catalyst is referred to as MoO$_3$/Al$_2$O$_3$ (sulph.) The unreduced unsulphided catalyst is referred to as MoO$_3$/Al$_2$O$_3$ (oxd.).

The experiments were carried out with a 1:10 molar mixture of amine and cyclohexane using a flow reactor operating at atmospheric pressure [9]. The reactor was made of a glass tube of radius 1 cm and length 30 cm. A spiral was wound coaxially so that the reactants, while passing through the spiral, were preheated to the same temperature as that of the catalyst before entering the catalyst zone. A 10-cm^3 amount of the catalyst was packed in the reactor between beds of Pyrex glass-wool. The liquid products were passed through a cooled condenser and collected in a trap kept cool in ice and the gaseous products were collected in a glass burette after bubbling through 0.1M hydrochloric acid. The liquid products were analysed by gas chromatography using 20% SE-

TABLE 1

Surface areas of the catalysts

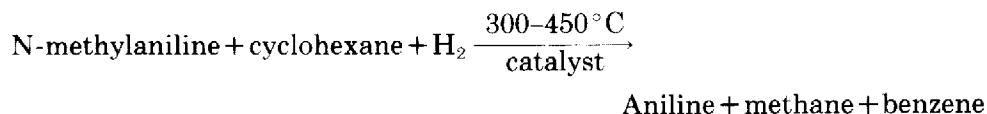| Catalyst	Surface area (m^2/g)
γ-Al$_2$O$_3$	120
12.4% MoO$_3$/γ-Al$_2$O$_3$	116
3% NiO–12.4% MoO$_3$/γ-Al$_2$O$_3$	108
3% CoO–12.4% MoO$_3$/γ-Al$_2$O$_3$	124

30 on Chromosorb W. Mixtures of known composition containing different amounts of aniline, N-methylaniline, benzene and cyclohexane were prepared. A calibration graph was drawn of peak area versus the number of moles of any particular component, and was used to calculate the exact amount of each component present in the product mixture. The ammonia formed as a result of nitrogen removal was determined volumetrically by titration with hydrochloric acid. Methane in the exit gas was identified by gas–liquid chromatography.

The sulphur removed as hydrogen sulphide during reaction was converted into lead sulphide and determined gravimetrically. The sulphur left behind on the used catalyst was oxidized to sulphur trioxide and dioxide and determined volumetrically.

Wherever necessary for the identification of products, mass, NMR and UV–visible spectrometry were used.

RESULTS AND DISCUSSION

Pure molybdena and the γ-alumina support individually showed negligible activity for the formation of aniline together with methane and benzene when compared with the supported molybdena catalyst:

$$\text{N-methylaniline} + \text{cyclohexane} + H_2 \xrightarrow[\text{catalyst}]{300-450\,^\circ C}$$

$$\text{Aniline} + \text{methane} + \text{benzene}$$

There are side-reactions accompanying the formation of aniline leading to small amounts of toluidine and N,N-dimethylaniline and varying amounts of high-molecular-weight products on MoO_3/Al_2O_3 (oxd.) and MoO_3/Al_2O_3 (red.). The high-molecular-weight products were detected as peaks appearing in the gas chromatogram with much higher retention times than N-methylaniline. These were isolated by column chromatography over silica as dark red portions which yielded semi-solid materials from which no single component could be isolated in a pure state. Their mass spectra showed molecular ions of m/z ranging from 207 to 235, which seem to arise from oxidative coupling of two molecules of N-methylaniline with or without further methylation.

These products seem to be the result of catalytic cracking on sites other than those responsible for hydrogenolysis. On the sulphided catalyst these byproducts are almost completely eliminated (Table 2). At the same time the hydrogenolysis activity of the sulphided catalyst is greater than that for the unsulphided catalyst. Further hydrogenolysis of aniline to benzene and ammonia also seems to take place to a small extent. Sulphidation seems to create sites responsible for hydrogenolysis and at the same time block the sites responsible for cracking.

TABLE 2

Effect of pretreatment on N-methylaniline hydrogenolysis in the presence of hydrogen and cyclohexane

Reaction temperature, 400 °C: contact time, 2.5 s; N-methylaniline, 0.01 mol h^{-1}.

Catalyst	Mol.-%[*]			
	Aniline	Ammonia	N-methylaniline unreacted	Other products[**]
MoO$_3$/Al$_2$O$_3$ (oxd.)[***]	33	–	32	35
MoO$_3$/Al$_2$O$_3$ (red.)[§]	35	–	43	22
MoO$_3$/Al$_2$O$_3$ (sulph.)[§§]	65	2.5	30	–

[*]Activity measured during 30–90 min of the reaction time.
[**]Mainly high-molecular-weight products; see text.
[***]Catalyst as prepared.
[§]Prereduced in hydrogen at 400 °C for 2 h.
[§§]Sulphided at 400 °C in hydrogen–hydrogen sulphide (9:1, v/v) for 3 h.

The results reported are activities measured during a reaction time of 30–90 min. The catalyst was found to maintain a steady-state activity between 30 and 90 min. This was checked by an independent experiment by collecting the product every 15 min. During the initial 30 min the activity is high and after 90 min the activity gradually decreases. The experiments were repeated at least three times and the values agreed to within ±3%. The catalyst regained its initial activity on resulphidation and the activity was maintained for about ten runs. Later it lost its activity and at this stage the catalyst was reoxidized by passage of carbon dioxide free air at 500 °C and then sulphided to restore the original activity.

The result in Table 3 show that the use of a combination of cyclohexane and hydrogen is better than the use of hydrogen or cyclohexane alone for the hydrogenolysis of N-methylaniline on MoO$_3$/Al$_2$O$_3$ (sulph.). Even in the absence of hydrogen and cyclohexane (with benzene being used as a diluent as it does not interact with N-methylaniline), N-methylaniline undergoes reaction to some extent. This can be attributed to cracking, which is also catalytic as in the absence of catalyst there is no reaction. Blank experiments were carried out without cyclohexane and benzene. The results obtained show that the presence of benzene does not affect the hydrogenolysis of N-methylaniline to any significant extent. It is observed that the overall conversion of N-methylaniline in the presence of benzene is the same as or slightly greater than that in the presence of cyclohexane. This can be attributed to the relatively higher adsorption of cyclohexane compared with benzene, which makes less catalyst surface available to N-methylaniline. As benzene does not interact with the catalyst surface more of the N-methylaniline is adsorbed, leading to more high-molecular-weight products.

TABLE 3

Hydrogenolysis of N-methylaniline in the presence of hydrogen and cyclohexane
Reaction temperature, 400 °C; contact time, 2.5 s; N-methylaniline, 0..01 mol h^{-1}; catalyst, MoO$_3$/Al$_2$O$_3$ (sulph.).

Reactants	Mol-%			
	Aniline	Ammonia	N-methyl-aniline unreacted	Other products[*]
N-Methylaniline + H$_2$ + cyclohexane	65	2.5	30	--
N-Methylaniline + N$_2$ + cyclohexane	45	--	41	14
N-Methylaniline + H$_2$ + benzene	55	Trace	30	15
N-Methylaniline + N$_2$ + benzene	40	--	35	25
N-Methylaniline + H$_2$	60	2.5	26	11.5
N-Methylaniline + N$_2$	42	1.5	40	16.5

[*]Mainly high-molecular-weight products; see text.

MoO$_3$/Al$_2$O$_3$ (sulph.) was found to lose part of the sulphur during the reaction and hence there was a decrease in activity for the formation of aniline as the reaction progressed, with a simultaneous increase in the formation of side-products. Resulphidation of the used catalyst restored its original activity.

Even with the presulphided catalyst, the presence of hydrogen sulphide in the reactant stream leads to a significant increase in the formation of aniline. This observation is rationalized by the suggestion that removal of sulphur from the catalyst during the reaction is prevented or compensated by the presence of hydrogen sulphide.

The effect of promoters such as cobalt and nickel, which could improve the denitrogenation of aniline on MoO$_3$/Al$_2$O$_3$, was studied.

As observed by Brunet and Perot [10], it is found that in the absence of hydrogen sulphide in the reactant stream sulphided NiO–MoO$_3$/Al$_2$O$_3$ is more stable than CoO–MoO$_3$/Al$_2$O$_3$. The extent of removal of sulphur during the reaction with different catalysts for between 0 and 90 min is given in Table 4.

Based on the removal of sulphur during the steady-state reaction conditions, a large loss of sulphur from the presulphided NiO–MoO$_3$/Al$_2$O$_3$ is observed when hydrogen alone is passed over the catalyst than when the reaction mixture is admitted together with hydrogen (Table 5). The difference in the loss of sulphur between the 30th and 90th minutes, although small, is real, as verified by repeated experiments. This indicates that the reactant prevents hydrogen from gaining access to the sulphur on the surface and the sulphur sites may be the active points for the hydrogenolysis of the C–N bond. The loss of sulphur observed between 0 and 30 min is the same in both experiments. This may be because some sulphur is loosely held on the surface and the amount of such loosely held sulphur is almost constant.

TABLE 4

Relative extents of sulphur removal on different catalysts under reaction conditions
Reaction temperature, 400 °C; contact time. 2.5 s; N-methylaniline, 0.01 mol h^{-1}.

Catalyst	Loss of total S in 0 90 min (%)	Initial S on the catalyst (g)
MoO_3/Al_2O_3(sulph.)	16.0	$3.55 \cdot 10^{-2}$
$CoO-MoO_3/Al_2O_3$(sulph.)	9.9	$5.10 \cdot 10^{-2}$
$Nio-MoO_3/Al_2O_3$(sulph.)	7.7	$5.70 \cdot 10^{-2}$

TABLE 5

Relative extents of sulphur removal when hydrogen with and without reactants is passed over the catalyst
Catalyst, $NiO-MoO_3/Al_2O_3$ (sulph.); reaction temperature, 400 °C; contact time, 2.5 s.

Reactants	Loss of total sulphur (%)	
	0-30 min	30–90 min
Hydrogen	6.7	3.0
N-Methylaniline + H_2 + cyclohexane	6.7	1.0

TABLE 6

Effect of presence of hydrogen sulphide in reactant stream on the hydrogenolysis of aromatic and aliphatic C-N bonds
Reaction temperature, 400 °C; contact time. 2.5 s; N-methylaniline, 0.01 mol h^{-1}.

Catalyst	Mol-%		
	Aniline	Ammonia	Unreacted N-methylaniline
MoO_3/Al_2O_3(sulph.)*	82	2.5	14
MoO_3/Al_2O_3(sulph.)**	65	2.5	25
$CoO-MoO_3/Al_2O_3$(sulph.)*	80	3.8	12
$CoO-MoO_3/Al_2O_3$(sulph.)**	71	3.9	21
$NiO-MoO_3/Al_2O_3$(sulph.)*	77	4.5	14
$NiO-MoO_3/Al_2O_3$(sulph.)**	69	5.4	17

*With hydrogen sulphide in the gas phase.
**Without hydrogen sulphide in the gas phase.

Table 6 shows that the introduction of promoters enhances the activity towards C N hydrogenolysis irrespective of whether the carbon is sp^2 or sp^3 hybridized. Incorporation of hydrogen sulphide in the reactant stream increases the hydrogenolysis of the $C(sp^3)-N$ bond (formation of aniline). The effect of hydrogen sulphide on the $C(sp^2)-N$ bond cleavage is negligible on the unpromoted and cobalt-promoted catalysts. On the nickel-promoted catalyst the activity for $C(sp^2)-N$ bond cleavage decreases when hydrogen sulphide is present in the gas stream. The activity with respect to $C(sp^2)-N$ bond cleavage follows the order $NiO-MoO_3/Al_2O_3$ (sulph.) $< CoO-MoO_3/Al_2O_3$ (sulph.) $< MoO_3/Al_2O_3$ (sulph.). In studies in which hydroprocessing of indole and o-ethylaniline [11] and pyridine [12] was investigated, similar trends were observed.

In order to verify the suggestion that the presence of hydrogen sulphide in the reaction stream has a promoting effect on the hydrogenolysis of the $C(sp^3)-N$ bond an inhibiting effect on the $C(sp^2)-N$ bond, hydrogenolysis of aniline and cyclohexylamine was studied on the $NiO-MoO_3/Al_2O_3$ catalyst. The results in Table 7 corroborate the suggestion.

It has already been reported that the presence of hydrogen sulphide favours denitrogenation. It is suggested that denitrogenation is catalysed by the hydrogen sulphide adsorbed on hydrogenating sites, namely sulphide anion vacancies [13]. Such behaviour was also observed in the hydrodenitrogenation of 1,2,3,4-tetrahydroquinoline [10], 7,8-benzoquinoline [7] and quinoline [14] on nickel-promoted catalysts. Based on the experimental results obtained in this work, it is suggested that denitrogenation of aliphatic amines [$C(sp^3)-N$ bond cleavage] is catalysed by the hydrogen sulphide adsorbed on hydrogenation sites and that of aromatic amines [$C(sp^2)-N$ bond cleavage] is catalysed

TABLE 7

Effect of addition of hydrogen sulphide on hydrogenolysis of aniline and cyclohexylamine
Reaction temperature, 450 °C; catalyst, $NiO-MoO_3/Al_2O_3$ (sulph.); amine*, $6.03 \cdot 10^{-3}$ mol h^{-1}.

Amine	Ammonia (mol-%)
Aniline**	11
Aniline***	17
Cyclohexylamine**	95
Cyclohexylamine***	82
N-Methylaniline**	7(75)[§]
N-Methylaniline***	11(67)[§]

*Because of the poor solubility of aniline in cyclohexane, comparison was made by carrying out experiments with a 1:20 molar mixture of amine and cyclohexane.
**With hydrogen sulphide in the reactant stream
***Without hydrogen sulphide in the reactant stream
[§]Values in parentheses refer to aniline (mol-%).

TABLE 8

Effect of temperature on the hydrogenolysis activity of N-methylaniline
Catalyst, Nio-MoO$_3$/Al$_2$O$_3$ (sulph.); contact time, 2.5 s.

Temperature (°C)	N-Methylaniline (mol h^{-1})	Mol-%			
		Aniline	Ammonia	N-Methylaniline unreacted	Other products[*]
400	0.01	69	5.4	17	8.6
450	0.0103	65	10.5	19	5.5
475	0.0106	52	12.6	17	18.4

[*]Mainly high-molecular-weight products; see text.

TABLE 9

Hydrogenolysis of N-methylaniline in the presence of hydrogen and cyclohexane
Reaction temperature, 400°C; contact time, 2.5 s; catalyst, NiO-MoO$_3$/Al$_2$O$_3$ (sulph); N-methylaniline, 0.01 mol h^{-1}.

Reactants	Mol-%			
	Aniline	Ammonia	N-Methylaniline unreacted	Other products[*]
Cyclohexane+H$_2$+ N-methylaniline	69	5.4	17	8
Cyclohexane+N$_2$+ N-methylaniline	51	2.7	24	22
Benzene+H$_2$+ N-methylaniline	60	4.5	20	15
Benzene+N$_2$+ N-methylaniline	38	1.8	30	30

[*]Mainly high-molecular weight products; see text.

more favourably by the sites which are exposed when some of the surface sulphide ions are removed. These could be Lewis acid sites.

As the temperature is increased from 400 to 475°C, the formation of ammonia increases and a corresponding decrease in aniline is observed (Table 8). The total N-methylaniline reacted remains almost constant with increase in temperature. This suggests that the conversion of N-methylaniline to aniline does not increase as much as the conversion of aniline to ammonia as the temperature is increased. One can attribute this to a lower energy of activation for the conversion of N-methylaniline compared with that for the formation of ammonia from aniline.

Table 9 shows that for the nickel-promoted catalyst also the use of cyclohexane and hydrogen for hydrogenolysis of N-methylaniline facilitates the hy-

drogenolysis of the C–N bond when the carbon is either sp^2 or sp^3 hybridized. This result may be compared with the similar effect found for the unpromoted catalyst (Table 3).

The hydrocarbon formed as a result of denitrogenation is benzene in the case of aniline, N-methylaniline and N,N-dimethylaniline and not cyclohexane. This fact was confirmed by using decalin as the diluent instead of cyclohexane. This leads to the conclusion that with aromatic amines the aromatic ring need not necessarily be hydrogenated for removal of nitrogen under mild conditions.

CONCLUSIONS

The use of a saturated hydrocarbon as a diluent facilitates C–N bond hydrogenolysis in the presence of hydrogen, irrespective of the carbon being sp^2 or sp^3 hybridized. The presence of hydrogen sulphide in the feed enhances the hydrogenolysis of the C(sp^3)–N bond and decreases the hydrogenolysis of the C(sp^2)–N bond. A nickel-promoted catalyst shows better activity for the hydrogenolysis of aromatic amines. Hydrogenation of aromatic ring is not a prerequisite for the removal of nitrogen.

ACKNOWLEDGEMENTS

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