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PROCESS FOR THE CATALYTIC SYNTHESIS
OF AMINES FROM ALCOHOL AND AM-
MONIA

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24 Claims. (Cl. 260—127)

This invention relates to the production of amines, and more particularly to a method of controlling the type of amines produced.

The catalytic synthesis of amines has been per-
5 formed by passing an alcohol vapor and anhy-
drous ammonia over a dehydrating catalyst, re-
sulting in the production of mixtures of the cor-
responding primary, secondary and tertiary
amines. It often happens, however, that only
10 certain amines are desired but, owing to the fact
that there was no known way of controlling the
synthesis so as to secure the production of the
desired amine only, the yield of the desired amine
was often poor and the cost therefore high.

15 It is therefore an object of this invention to
provide an improved process for the catalytic
synthesis of amines from alcohols and ammonia,
which enables the reaction to be directed selec-
tively so that the formation of an undesired
20 amine may be inhibited.

It is another object of this invention to provide
an improved process for the catalytic synthesis
of amines from alcohols and ammonia, which
enables the reaction to be directed selectively
25 to the formation of any one of the mono-, di-,
or tri-amines desired, at the same time inhibiting
nearly or entirely the formation of the other
two.

30 With the above and other objects in view, which
will be apparent as the description proceeds, I
have set forth my invention in the following spec-
ification and have indicated certain specific em-
bodiments of my invention by way of illustration
and not as a limitation.

35 It has been found that given the optimum con-
ditions of pressure, temperature, and space vel-
ocity, the molecular ratio of alcohol to ammonia is
the most important factor influencing yield, and
proportion of primary, secondary, and tertiary
40 amines in the product. As this ratio is increased
the total conversion increases. At low ratios,
c. g., 1 to 4, primary amine is the major product,
while at a ratio of about 3 to 1 primary amine dis-
appears, the product consisting of secondary and
45 tertiary amines, tertiary being formed in the
larger amounts.

According to my invention, secondary amine
may be formed selectively and nearly to the ex-
50 clusion of the other two by operating with a high
ratio of alcohol to ammonia, thus eliminating
the formation of primary amine, and inhibiting
formation of tertiary amine by passing a certain
amount of this product over the catalyst with
the alcohol. The equilibrium is thus shifted in
55 the direction of secondary amine formation, re-

sulting in a product consisting almost entirely of
secondary amine.

The selective formation of primary amine is
accomplished by operating at a very low ratio of
alcohol to ammonia, and recirculating any sec-
5 ondary or tertiary amine produced, with the re-
sult that the product consists almost entirely of
the primary compound.

The selective formation of tertiary amine is
accomplished by operating at a high ratio of 10
alcohol to ammonia and recirculating any lower
amines produced, with the result that the prod-
uct consists almost entirely of the tertiary com-
pound.

Although any desired dehydration or amination 15
catalyst, such as alumina or thoria, may be used
in this process, I prefer alumina prepared in gel
form by the hydrolysis of aluminum ethoxide in
aqueous ethyl alcohol solution as follows:

A saturated solution of aluminum ethoxide 20
in absolute ethyl alcohol is prepared by boiling
under a reflux condenser. After cooling, the
clear solution is decanted or filtered from the ex-
cess ethoxide or alumina and the solution is
25 then poured rapidly into an equal volume of
ethyl alcohol containing 2% of water by volume.
The mixture sets to a gel in 1 to 2 minutes, after
which it is allowed to stand in the air for several
days or until no more alcohol is squeezed out.
30 Considerable shrinkage occurs during this period,
the alcohol which comes out being drawn off
from time to time. The gel is then dried out
slowly over a period of about three days, start-
ing at about 50° C. and increasing the tem-
35 perature gradually to about 110° C. After dry-
ing the gel is roasted at 500° to 600° C. for eight
hours by which time it has acquired the form
of very hard, clear granules. The catalyst is then
ready for use after screening to a convenient
40 size, preferably 8 to 14 mesh.

Example 1

Absolute methanol at the rate of 0.75 to 1.5 cc.
per cc. of catalyst per hour, together with suf-
45 ficient anhydrous ammonia to give a molecular
ratio of methanol to ammonia of 3 to 4 methanol
to 1 of ammonia, is preheated to 300° to 350° C.,
and passed over an alumina gel catalyst heated
to 400° to 500° C., the preferred temperature be-
50 ing 450° C. Under these conditions an initial
conversion to total amines of 85% of the am-
monia input is obtained, of which 57% is tertiary
amine and 28% secondary, with no primary.
The tertiary amine is then separated from the
55 secondary by distillation and recirculated over

the catalyst with fresh methanol and ammonia, after which only about 8% of tertiary is formed, the conversion to secondary being from 45 to 50% of the ammonia.

Example 2

Monomethylamine is formed with only traces of di- and tri-methylamine, by passing methanol and ammonia, in the ratios of from 1:1 to 1:5 over alumina gel, at a rate similar to that used in Example 1. The vapors are preheated to about 350° C. and the catalyst is kept at 450° C. About 13.5% of the ammonia is thus converted to primary amine, secondary and tertiary amines being formed in amounts representing 7.5 and 10.5% respectively of the ammonia. The secondary and tertiary amines are then separated from the primary amine and recirculated over the catalyst with fresh methanol and ammonia, thus increasing the proportion of primary amine and materially decreasing the proportion of secondary and tertiary amines present.

Example 3

If it is desired to control the process of the synthesis of amines so as to obtain tertiary amines as a major constituent, this can be done by operating at a high ratio of methanol to ammonia. Methanol and ammonia in the ratio of 3 to 1 are passed over alumina gel at 450° C. and a space velocity of 1 cc. per cc. of catalyst per hour, producing a conversion of ammonia to methylamines of about 85%. This product consists of secondary and tertiary amines in the ratio of about 1 to 2, representing conversions of about 28% and 57%, respectively. Only traces of primary amine are formed. By recirculating the secondary amine the further production of secondary amine is inhibited and the relative proportion of tertiary amine is increased.

This invention is applicable to the synthesis of aliphatic amines such as methyl, ethyl or butyl amines; to the aromatic amines such as aniline, the toluidines or benzyl-amine; and to mixed alkyl-aryl amines such as monomethyl, dimethyl, monoethyl or diethyl aniline.

It will therefore be apparent that I have invented a new and useful method of making amines in which the production of an undesired amine or amines is inhibited by adding the undesired amine or amines to the reaction mixture.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended patent claims.

I claim:

1. In the process of making amines by the catalytic synthesis in the vapor phase of primary alcohols and ammonia, the method of controlling the relative quantities of primary, secondary and tertiary amines produced which consists in adding the undesired material to the reaction mixture to inhibit the production of said undesired material.

2. The process of claim 1 in which the catalyst is an alumina gel.

3. The process of making amines by the catalytic synthesis in the vapor phase from primary alcohols and ammonia, which consists in adding amines having a higher degree of alkylation than a given amine to decrease the relative proportion of said amines having a higher degree of

alkylation than a given amine produced and to increase the relative proportion of said given amine produced.

4. The process of making amines by catalytic synthesis in the vapor phase primary alcohols and ammonia in which the formation of tertiary amine is inhibited by passing tertiary amine over an amination catalyst with the alcohol and ammonia.

5. The process of making amines by catalytic synthesis in the vapor phase primary alcohols and ammonia in which a high ratio of alcohol to ammonia is used and in which the formation of tertiary amine is inhibited by passing tertiary amine over an amination catalyst with the alcohol and ammonia.

6. In the process of making aliphatic amines by catalytic synthesis in the vapor phase of primary aliphatic alcohols and ammonia, the method of controlling the relative quantities of primary, secondary and tertiary amines produced which consists in adding the undesired amine to the reaction mixture to inhibit the production of the undesired amine.

7. The process of making aliphatic amines by catalytic synthesis in the vapor phase of primary aliphatic alcohols and ammonia, which consists in adding amines having a higher degree of alkylation than a given amine to decrease the relative proportion of said amines produced and to increase the relative proportion of said given amine produced.

8. The process of making aliphatic amines by catalytic synthesis in the vapor phase of primary aliphatic alcohols and ammonia in which the formation of tertiary amine is inhibited by passing tertiary amine over an amination catalyst with the alcohol and ammonia.

9. The process of making aliphatic amines by catalytic synthesis in the vapor phase of primary aliphatic alcohols and ammonia in which a ratio of alcohol to ammonia of about three to one is used and in which the formation of tertiary amine is inhibited by passing tertiary amine over an amination catalyst with the alcohol and ammonia.

10. The process of making amines which consists in passing methanol and ammonia in the vapor phase over an amination catalyst to form a high proportion of secondary and tertiary amines relative to the quantity of primary amine formed, separating the tertiary amine from the secondary amine by distillation, and recirculating the tertiary amine over the catalyst with fresh methanol and ammonia.

11. The process of making amines which consists in passing methanol and ammonia in the vapor phase over an amination catalyst in the ratio of three to four parts of methanol to one part of ammonia to convert 85% of the ammonia into secondary and tertiary amines, separating the tertiary amine from the secondary amine by distillation, and recirculating the tertiary amine over the catalyst with fresh methanol and ammonia.

12. The process of claim 11 in which the methanol is passed over the catalyst at the rate of 0.75 to 1.5 cc. per cc. of alumina gel per hour, and in which the reaction mixture is preheated to 300° to 350° C. and the catalyst is heated to 400° to 500° C.

13. Process for the production of methylamine which comprises passing a gaseous mixture comprising one part methanol and about one to about five parts ammonia at a temperature of about

400° to about 500° C. over metallic oxide dehydrating catalysts.

14. Process for the production of methylamine which comprises passing methanol with a molecular excess of ammonia at a temperature of about 400° to about 500° C. and at a space velocity of about .75 to about 1.5 cc. of absolute methanol per cc. of catalyst per hour over metallic oxide dehydrating catalysts.

15. Process for the production of methylamine which comprises passing a gaseous mixture comprising one part methanol and about one to about five parts ammonia at about 400° C. over metallic oxide dehydrating catalysts.

16. Process for the production of methylamine which comprises passing a gaseous mixture comprising one part methanol and about one to about five parts ammonia at about 400° C. and at a space velocity of about 1100 cc. of gaseous reactants per cc. of catalyst per hour over metallic oxide dehydrating catalysts.

17. A process for the production of methylamine, the steps which comprise passing a mixture of methanol with a molecular excess of ammonia at a temperature of about 400° to about 500° C. over catalysts comprising aluminium oxide.

18. In a process for the production of methylamine, the steps which comprise passing a mixture of methanol and ammonia at a temperature of about 400° to about 500° C. and at a space velocity of about .75 to about 1.5 cc. of absolute methanol per cc. of catalyst per hour over catalysts comprising aluminium oxide.

19. In a process for the production of methylamine, the steps which comprise passing a mixture of methanol and ammonia at about 400° C. and at a space velocity of about 1100 cc. of gaseous

reactants per cc. of catalyst per hour over catalysts comprising aluminium oxide.

20. In a process for the production of methylamine, the steps which comprise passing a mixture of methanol and ammonia at a temperature of about 400° to about 500° C. over catalysts comprising dehydrated aluminium hydroxide.

21. In a process for the production of methylamine, the steps which comprise passing a mixture of methanol and ammonia at a temperature of about 400° to about 500° C. and at a space velocity of about .75 to about 1.5 cc. of absolute methanol per cc. of catalyst per hour over catalysts comprising dehydrated aluminium hydroxide.

22. In a process for the production of methylamine, the steps which comprise passing methanol and a molecular excess of ammonia at a temperature of about 400° to about 500° C. and at a space velocity of about .75 to about 1.5 cc. of absolute methanol per cc. of catalyst per hour over catalysts comprising dehydrated aluminium hydroxide.

23. In a process for the production of monomethylamine, the steps which comprise passing methanol and a molecular excess of ammonia at a temperature of about 400° to about 500° C. and at a space velocity of about .75 to about 1.5 cc. of absolute methanol per cc. of catalyst per hour over catalysts comprising dehydrated aluminium hydroxide.

24. Process for the production of methylamine which comprises passing methanol with a molecular excess of ammonia at temperatures ranging from 400° to 500° C. over metallic oxide dehydrating catalysts.

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