



Contents List available at VOLKSON PRESS

New Materials and Intelligent Manufacturing (NMIM)

DOI : <http://doi.org/10.26480/icnmim.01.2018.191.194>Journal Homepage: <https://topicsonchemeng.org.my/>

ISBN: 978-1-948012-12-6

PROGRESS IN THE HYDRO-AMINATION OF ALCOHOLS

Huan Wang¹, Xin Li ², Jibo Zhang^{1*}¹Institute of Petroleum and Chemical, Jilin Institute of Chemical Technology, Jilin Jilin 132022, China.²School of Chemistry and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Jilin Jilin 132022, China.*Corresponding Author Email: 465419341@qq.com

This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited

ARTICLE DETAILS

ABSTRACT

Article History:

Received 26 June 2018

Accepted 2 July 2018

Available online 1 August 2018

Aliphatic amine is an important intermediate of fine chemical industry. It is main used in pharmaceutical, foodstuff, cosmetics and fine chemicals industries. It has a variety of synthetic routes. The Progress in the hydro-amination of alcohols to aliphatic amines at home and abroad were reviewed in this paper. The reaction mechanism of alcohol amination process of fatty alcohols and several synthesis methods of aliphatic amines was introduced. The influence of aliphatic amines production was discussed such as catalyst type and process condition and so on. According to actual production status, we provide reference for the development of production process of alcohol amination.

KEYWORDS

Aliphatic amines, amination, catalyst, process.

1. INTRODUCTION

Aliphatic amines and derivatives are an extremely important chemical raw material and intermediate, which can be widely used in various fields of the chemical industry. For example, lower aliphatic amines are mainly used in pesticides, pharmaceuticals, dyes, fuels, surfactants, etc.; higher aliphatic amines and their derivatives are mainly used as fabric softeners, surfactants, mineral flotation agents, oil additives, etc.; In addition, piperazine series compounds in cyclic amines are important pharmaceutical intermediates, and polymethylpolyamines such as tetramethylethylenediamine are important polyurethane foaming and curing catalysts. Obviously, It is significant that research and develop aliphatic amines process methods and catalysts.

1.1 Aliphatic amine synthesis process methods

The presence of lower aliphatic amines has not been found in natural. Industrially produced lower aliphatic amines are produced by synthetic methods, while higher aliphatic amines are produced from natural oils or synthetic raw materials. In fact, there are many complex synthetic processes that correspond to the types of amines and derivatives. There are many methods for synthesizing aliphatic amines in industry, for example, halogenated hydrocarbon ammonolysis, α -olefin amination, aldehyde amination hydrogenation, cyanamide reduction, alcohol amination etc.

Hydrogen halide and ammonium salt have been produced in halogenated hydrocarbon ammonolysis, then ammonium salt will produce sodium chloride (NaCl) after reacting with caustic soda, which will cause serious equipment corrosion and environmental pollution.

α -Olefin amination is more simple and lower investment process. However, the process is relatively harsh Which needed more demands at this stage. It needs to be carried out under higher temperature and higher pressure. there is still a major breakthrough in catalyst research if we want to achieve industrialization.

The process of Aldehyde amination hydrogenation is mild, and the yield is higher. However, It is used only for the production of fatty amines that are

readily available as raw materials. The cost of raw materials for Cyanide reduction is higher. It caused serious pollution Which was used reducing agents. So the process has been limited. Alcohol amination of raw materials is cheaper and easier to obtain less pollution. Compared with other methods, it is the most powerful method in terms of process, cost and quality. It is suitable for large-scale continuous synthesis of aliphatic amines process route.

2. ALCOHOL AMINATION REACTION CONDITIONS

2.1 Process for Hydrogenation Amination of Amines by Alcohols

The process for hydro-amination of alcohols to aliphatic amines: First, Hydro pressure; then the raw materials are mixed and vaporized into a reactor equipped with a catalyst; Dehydrogenation, Amination, Hydrogenation, It is performed to generate amine compounds. By reacting alcohols with primary amines, secondary amines, and ammonia, tertiary amines, primary amines, and secondary amines can be synthesized. It is a widely used method to synthesize amines. As shown in Figure 1.

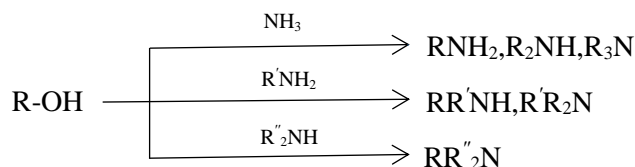


Figure 1: Alcohol Amination Synthesis of Alkylamines

2.2 Reaction mechanism

The raw material and liquid ammonia are preheated by the heater, and the liquid is converted into a gas, then the gas is reheated to the required initial temperature of the reaction. In the hydrogen state, then the catalyst catalyzed. There are the following reaction steps that according to the difference activity of molecular radicals. First, the alcohol is dehydrogenated to aldehyde; second, the aldehyde hydrogen atoms are replaced by amino groups; then, the imine is formed. The imine is an unstable intermediate product. It hydrogen to amine. The reaction mechanism is inferred as shown in Figure 2.



Figure 2: Presumed amination reaction of alcohols

3. CATALYST RESEARCH AND DEVELOPMENT

The benefits of the synthesis of alcohols in the hydroamination reaction depend on the performance of the catalyst. Catalyst development is the core. The catalyst is divided into active components, co-catalysts and supports. Due to the different reaction conditions of catalyst performance, pressure, temperature, and catalyst dosage, it has a great influence on the quality of equipment and amines. Therefore, the research focus is to develop low-temperature and low-pressure catalysts with high activity,

high selectivity, and good stability.

3.1 The composition of the catalyst

Most of the alcohol amination reaction catalysts have been reported in patents. The composition is mainly Cu, Ni, Co, Cr and other elements. otherwise, Ba, Mg, W, Mo, Sn and rare earth elements. Table 1 summarized the performance of catalysts with different components [1].

Table 1: Title of the Table

Active component	support	activity	selectivity
Cr ₂ O ₃	γ-Al ₂ O ₃	-	+
Fe ₂ O ₃	-	-	-
CoO	silica gel	++	+++
CoO	γ-Al ₂ O ₃	++	+++
CoO/La ₂ O	-	++(++)	+++(++)
CoO/MoO ₃	γ-Al ₂ O ₃	++(+)	++(+)
Ni (Raney)	-	+++	++
NiO	silica gel	+++	+++
NiO	γ-Al ₂ O ₃	+++	+++
NiO/CuO	silica gel	+++ (+++)	+++ (++++)
Ru	acticarbon	+	+
Rh	acticarbon	+	+
Rd	acticarbon	+	+
Pd	γ-Al ₂ O ₃	+	++
Pt	acticarbon	+	+
Pt	γ-Al ₂ O ₃	+	++
CuO	γ-Al ₂ O ₃	+++	+++++
CuO	silica gel	+++	+++++
CuO	kaoline	+++	+++++
CuO/NiO	silica gel	+++ (+++)	+++++ (+++)
CuO/Cr ₂ O ₃	silica gel	+++ (++)	+++++ (++++)
CuO/Cr ₂ O ₃	γ-Al ₂ O ₃	+++ (++)	+++++ (++++)
CuO/Cr ₂ O ₃	-	+++ (++)	+++++ (++++)
CuO/ZnO	-	+++ (++)	+++ (++)
ZnO	-	-	-
ZnO/Cr ₂ O ₃	-	- (-)	- (+)
γ-Al ₂ O ₃	-	+	++++
α-Al ₂ O ₃	-	-	++

P.S.:1. The brackets indicate performance trends when the second component mass fraction increases ;

2.The catalyst is used after activation ;

3.Activity and selectivity: - ≤0.2,++≥0.4,+++≥0.6,++++≥0.8,+++++≥0.9.

Obviously, from the table we known: Catalysts with Cu as the main component have better activity and selectivity. However, catalysts with Cu as the active component have poor reactivity. We must be considered for metal recombination. Cu/Ni or Cu/Cr have better compounding effect. The supports could be Al₂O₃, SiO₂, Celite, molecular sieves, etc. This kind of catalyst is usually prepared by dipping or coprecipitation method.

In order to increase the selectivity of the catalyst, the atomic ratio of the active component must be matched. A studied the influence of the Cu/Ni atomic ratio on the Cu-Ni catalyst [2]. The relative activity of the catalyst increased when the Ni content increases. Abeyu discovered that the catalyst has higher activity when n(Cu):n(Ni)=4:1;And he also found that had high activity and selectivity at low temperature.

3.2 Catalyst support

Another way to improve catalyst selectivity is to find suitable supports. There are many compounds that can be selected as amination catalyst supports, but they must have a certain degree of alkalinity, such as Al₂O₃, ZnO, SiO₂, alumino silica gel (SiO₂-γ-Al₂O₃) etc.

The action of the supports may change the size and shape of the metal

particles, and the electronic interaction between the metal and the support can also change the size of the metal particles [3]. On the other hand, It can reduce costs and have a degree of economic benefits after adding the supports.

Some researchers investigated the synthesis of cyclohexylamine using CuO/NiO catalyst [4]. The bentonite and phosphoric acid treated γ-Al₂O₃ as supports. They found that the activity of γ-Al₂O₃ pretreated with phosphoric acid as support is significantly higher than bentonite. The reason may be that the pretreatment of phosphoric acid improves the microporous structure of the support, and it may be that part of the oxygen atoms on the Al₂O₃ skeleton are replaced by P.

A group researchers investigated whether the type of catalyst support that used for the hydrogenation of ethanol to produce ethylamine would affect the performance of Co catalysts (at 160°C,1.75MPa, ethanol space velocity 0.3h⁻¹) [5]. The also investigated whether the type of catalyst support that used for the hydrogenation of ethanol to produce ethylamine would affect the performance of Co catalysts (at 160°C,1.75 MPa, ethanol space velocity 0.3h⁻¹) [5]. The results of the different supports of the catalyst are listed in Table 2.

Table 2: Influence of support in ethanol dehydrogenating reaction

Catalysts	Amines Yield,%			
	Total Yield	Monoethylamine	Diethylamine	Triethylamine
SiO ₂	78.4	49.5	41.1	9.4
γ-Al ₂ O ₃	47.2	46.5	45.6	7.9
SiO ₂ -1Al ₂ O ₃	76.6	50.5	41.6	7.9
SiO ₂ -4Al ₂ O ₃	70.1	51.5	39.5	9.0
SiO ₂ -9Al ₂ O ₃	63.5	52.6	37.5	9.9

As can be seen from the table 2, the yield and selectivity of the Co/SiO₂ are higher than other supports, and the performance is best.

Other researchers investigated the influence of supports on the amination

reaction [6]. They used Ni-Cu composite metal as the active component, and mordenite, γ-Al₂O₃, and HZSM-5 as supports (at 230°C, 10MPa, and Glycol space velocity 0.2h⁻¹). The results are listed in Table 3.

Table 3: Effects of catalyst support on amination reaction

Supports	Conversion of EG,%	Yield of PIP,%	Selectivity of products,%			
			EDA	PIP	NEP	DEG
M	42.63	32.00	3.79	75.06	12.13	9.02
HZSM-5	44.38	29.65	7.64	66.82	7.66	16.39
γ-Al ₂ O ₃	40.52	23.71	2.85	58.51	21.43	15.48

From the table 3, different supports have less effect on the conversion of ethylene glycol, but it has a great influence on the product conversion rate. The selectivity of the product aminoethylpiperazine and diethylene glycol was higher, and the yield of piperazine was lower when the γ-Al₂O₃ as support. The selectivity of piperazine is higher when the mordenite as support. The selectivity of ethylenediamine and diethylene glycol as by-products is higher, and the selectivity of piperazine is lower when the HZSM-5 as support.

3.3 Co-catalyst

The co-catalyst also called catalytic accelerator and it occupies a relatively small amount in catalyst. It has no or little catalytic activity, but it can greatly increase the activity, selectivity and life of the main catalyst.

Some researchers added Ba as a co-catalyst in catalyst that Cu-Ni as active components and CaCO₃ as support [6]. They examined the performance of the catalyst and studied the reaction mechanism [6,7]. As a result, it was found that the addition of Ba can suppress the reduction of Ni in oxidation state of the catalyst, that make Ni maintained a relatively high valence. thereby it can effectively increase the selectivity of the catalyst. The catalytic performance of Cu-Ni-Ba catalyst is obviously better than that of Cu-Ni catalyst.

The characteristics of the amination catalysts are hydrogenation-dehydrogenation activity and proper alkalinity, which are similar to rare earth elements. The rare earth elements La, Nd and Gd were introduced into the alcohol amination catalyst [2]. The results showed that different rare earth elements showed different effects: Nd has a weak inhibitory effect, while La and Gd have a weak promoting effect. However, the promotion effect of rare earth elements is much weaker than Ni. Rare earth elements play a more important role in regulating the activity of catalysts, inhibiting side reactions and increasing selectivity.

3.4 Stability of the catalyst

The stability of catalyst is also the problem of catalyst deactivation. From the point of view of production, the importance of stability is equivalent to selectivity. There are many factors that affect the stability of catalysts: Impurities; reaction conditions; Changes in the composition and structure of the catalyst during the reaction process, Such as sintering, valence state change, group shunting loss etc.

Baiker and other studies found that increasing the partial pressure of hydrogen in the reaction system is beneficial to the inhibition of the formation of nitrogen compounds on the surface of the Cu/support catalyst [8]. Hydrogen can effectively prevent the deactivation of the catalyst.

Another important factor for the deactivation of the catalyst is the sintering. Lif and other studies have found the deactivation of the Ni catalyst supported by Al₂O₃ in the hydrogen atmosphere. It is found that the inactivation of the Ni catalyst is due to the sintering of the migration of the active component Ni.

3.5 The method of preparation of catalyst

The methods of preparing alcohols amination catalysts include dip-

molding, co precipitation, sol-gel and microemulsion. I will focus on dip-molding. First, the support which has been formed in a certain proportion of nitrate solution in a certain temperature condition is dipping for a period of time, then the support is taken out and drained. Second, the drained carrier is dried in an oven for a period of time. The dried carrier is placed in an electric resistance furnace and calcined. After a certain time, it is taken out for cooling. finally, the catalyst is obtained. It is the simplest process, No waste water and waste residue. NO_x waste gas can be absorbed.

4. INFLUENCE OF PROCESS CONDITIONS

The process conditions for prohydroamination of alcohols directly affect the quality of the reaction, such as temperature, pressure and ratio of raw materials etc. Generally, an excellent catalyst has its matching process conditions. In other word, different catalysts have different requirements for process conditions, However, there is a broad range of major process parameters.

4.1 Reaction temperature

Both in terms of kinetics and thermo dynamics, for the hydroamination amination reaction of alcohols that the higher the reaction temperature, the better. However, in the presence of side reactions, the reaction order of side reactions is higher than that of the main reaction, so the high temperature favors side reactions and the selectivity of the reaction decreases, so the reaction temperature has a direct impact on the amination reaction of alcohols. However, the reaction sequence of the side reaction is higher than the main reaction, the high temperature is better for side reactions and the selectivity of the reaction is decreased. So the reaction temperature has a significant impact on the amination reaction of the alcohol.

The suitable amination temperature is 210~225°C. The finer temperature control points should be carefully determined based on the performance of the catalyst. At a low temperature, the hydrogenation capacity of the catalyst is insufficient, and the reaction rate is slow. At a high temperature, the hydrogenation ability of the catalyst is better. The initial amination speed was faster, then the reaction slowed down in later stage. It is because the alcohol content of the material is tailed, it cannot reach the end of the reaction quickly.

Therefore, from the perspective of reducing costs and improving quality, Too high or too low reaction temperature will have adverse effects. It is necessary to seek a balance between catalytic activity and selectivity.

4.2 Reaction pressure and ratio of ammonia to alcohol

The amination reagents commonly used in alcohols amination is ammonia. When ammonia is used as an amination reagent, intermediate amines with higher activity than ammonia can be produced. The reaction product becomes very complicated and the post-processing is difficult.

Therefore, in order to increase the selectivity of the reaction, the higher pressure and ammonia-to-alcohol ratio are required. Some researchers investigated the reaction of ethanolamine aminating to ethylenediamine using Ni catalyst [9]. It is found that the selectivity of ethylenediamine can reach 70% ~ 90% when the ammonia pressure is 13~17MPa. When ammonia pressure is less than 8MPa (ammonia to alcohol ratio decreased),

the selectivity of ethylenediamine is only 40%.

It can be seen that in the amination reaction of diols, when the ammonia alcohol is relatively low, the cyclic amine is easy to get; and the selectivity to the diamine is relatively poor.

4.3 Hydrogen partial pressure

When metal catalysts are used in alcohols amination, the alcohol compounds may undergo dehydrogenation/hydrogenation, thus the pressure of hydrogen has a significant effect on the reaction results. The main function of hydrogen is to increase the selectivity of reaction and maintain the activity of catalyst.

In the study of ethanolamine hydrogenation reaction, it is found that the higher hydrogen pressure is beneficial to the formation of cyclic amines, and the lower hydrogen pressure is beneficial to the formation of diamines [10-13]. However, if the hydrogen pressure is too low, it will easily cause the catalyst to deactivate. Therefore, it is very important to select the appropriate hydrogen pressure for a particular reaction.

In addition, there are others factors that have a great effect on the alcohols amination reaction, For example, Molar ratio of reactants, Temperature, Time, etc [14,15]. All of these need to be systematically investigated to a specific reaction.

5. CONCLUSION

The synthesis of aliphatic amine by alcohols amination has been studied and explored at home and abroad, and it has reached a mature and stable stage. The key technology of the process is the study of catalysts. But in recent years, The reports on amination of alcohols are mostly patent and there is no major breakthrough in basic research.

We should strengthen the in-depth study of the reaction mechanism of alcohols amination. In the aspect of catalyst, we should strengthen the research on the performance of catalyst under microcosmic condition. Selecting high-activity, high-selectivity catalysts and improving catalyst stability. So We should improve and optimize the existing process, and develop a new technology for the production of aliphatic amines with energy saving, environmental protection and low consumption.

ACKNOWLEDGEMENTS

I would like to thank Professor Jibo Zhang for guiding me in academics, so that I can successfully complete this paper. I would like to thank the teachers of the Institute of Petroleum and Chemical for their suggestions and help me to have a great improvement in academics. Thanks the students in my class for their help in my life.

REFERENCES

- [1] Baiker, A. 1981. Catalytic amination of aliphatic alcohols. The role of hydrogen as inhibitor for catalyst deactivation [J]. *Industrial & Engineering Chemistry Product Research and Development*, 20, 615-618.
- [2] Fushan, Y., Yinguang, C., Xuemin, L. 1996. Amination of fatty alcohols [J]. *Daily Chemical Industry*, (4), 1-4.

[3] Atochem. 1990. Process for manufacturing amines from olefins: US.4937383[p], 06-26.

[4] Yangxin, L., Chao, Q., Jianqing, L. 2004. Synthesis of Cyclohexylamine with CuO/NiO/ γ -Al₂O₃ Catalyst [J]. *Chemical Reaction Engineering and Technology*, 20 (4), 134-138.

[5] Zhenshan, W., Shan, Y.J., Hongli, Z. 2001. Selection of Catalyst Supports for Dehydroamination of Alcohol to Make Lower Aliphatic Amines [J]. *Journal of Fuel Chemistry and Technology*, 29, 109-111.

[6] Zhen, Y., Feixiang, G., Yonghong, Q. 2016. Catalyst and Amination Process for the Synthesis of Piperazine from Ethylene Glycol [J]. *Chemical Reaction Engineering and Technology*, 32 (6), 570-274.

[7] Ping, T., Qiuxiao, L. 2003. Effects of Element Mole Ration on the Properties of the Cu-Ni Catalysts for the Amination of Fatty Alcohols [J]. *Fine Chemicals*, 32 (2), 17-19.

[8] Baiker, A., Kijenski, J. 1985. Catalytic synthesis of higher aliphatic amines from the corresponding alcohols [J]. *Catalysis Reviews*, 27 (4), 653-697.

[9] Lichtenberger R. Weiss F. 1962. Process of Making Ethylenedamine. United States Patent Office, 260-585. US3068290.

[10] Hironaka, T., Nagasaki, N., Hara, Y. 1994. Process for Producing an Ethylenamine. United States Patent, US5321160.

[11] Lif, J., Skoglundh, M., Lowendahl, L. 2002. Sintering of nickel particles supported on γ -alumina in ammonia. *Applied Catalysis A*, 228 (1-2), 145-154.

[12] Zhigang, Y., Wei, D., Baoqin, L., Guiying, Z. 2016. Research advance of catalytic amination of alcohol [J]. *Chemical Technology Market*, (11), 51-56.

[13] Hubert, H.J., Klaus, D., Tillmetz, Vinnun, O. 1986. Method for making amines [P]. US:4621158, 11-04.

[14] Sewell, G., Conner, C.O., Steen, E.V. 1995. Reductive amination of ethanol with silica-supported cobalt and nickel catalysts [J]. *Applied Catalysis A*, 125 (1), 99-112.

[15] Jianhua, G. 2010. Research progress of fatty amine processes and catalysts [J]. *Journal of Chemical Industry & Engineering*, 31 (1), 44-47.

ABOUT THE AUTHORS

Huan Wang (1990-), She is a Master graduate student. She is mainly engaged in the study of the Alcohol Hydrolysis Amination Process. Email: 1169316516@qq.com.

Xin Li (1993-), He is a Master graduate student. He is mainly engaged in the research of amine catalysts. Email: 10344826@qq.com.

Jibo Zhang (1969-), He is a professor at the Jilin Institute of Chemical Technology. He is mainly engaged in chemical process development and fine chemical development, etc. Email: 465419341@qq.com.

