

Research on the Catalytic Dehydrogenation and Amination of Benzyl Alcohol to Prepare Benzonitrile

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Abstract—Benzonitrile, a high-value organic intermediate naturally present in peanuts, hazelnuts, cocoa, and dairy products, is widely used in pharmaceuticals, agrochemicals, dyes, and fine chemical industries. The growing market demand for benzonitrile derivatives has driven the urgent need for more efficient synthesis methods. Early approaches, such as extraction from coal tar or dry distillation of ammonium benzoate, suffered from low yields and collection challenges. Current industrial routes rely on cyanidation methods, which face significant drawbacks including cyanide-containing wastewater generation, severe pollution, high treatment costs, energy consumption, and unwanted side reactions. Recently, oxidative ammoxidation of aromatic primary alcohols to corresponding nitriles has emerged as a research hotspot, with the development of efficient heterogeneous catalysts being critical for addressing the challenges of dehydrogenation-ammoxidation synergy and selectivity control. This study proposes a green catalytic process for one-step synthesis of benzonitrile via dehydrogenative ammoxidation of benzyl alcohol, emphasizing efficiency, cost-effectiveness, and simplified technology. By comparing the catalytic activity and catalytic selectivity of various load catalysts, Cu/γ-Al₂O₃ was finally selected as the best catalyst for this reaction. Reaction conditions, including temperature and gas atmosphere, were further optimized. Secondly, the physical and chemical properties were studied in depth by using X-ray powder diffraction (XRD), N₂-physical adsorption and desorption (BET), scanning electron microscopy (SEM), pyridine infrared (Py-IR), NH₃-TPD and other characterization methods. A plausible reaction pathway for benzyl alcohol ammoxidation was also proposed. This work provides a novel non-noble-metal-catalyzed route for industrial-scale benzonitrile production, offering a sustainable alternative to conventional methods.

Keywords— Benzyl alcohol; Ammonia; Benzonitrile; Dehydrogenative-ammoxidation; Cu/γ-Al₂O₃.

I. INTRODUCTION

Benzonitrile, also known as benzyl nitrile, is a colorless oily liquid, slightly soluble in cold water, soluble in hot water, soluble in ethanol and ether, with the smell of almonds, with a density of 1.01 g/cm³ (20 °C), a melting point of -12.8 °C, and a boiling point of 190.7 °C. The flash point is 71.7 °C. Benzonitrile is a high value-added organic intermediate, which is determined by the unique chemical properties of the cyano group in this type of compound: the cyano group, as an important functional group, can not only be reduced to an amino group and hydrolyzed to a carboxyl group, but also participate in a variety of key chemical reactions. In the field

of organic chemistry, benzonitrile compounds have become an important class of organic compounds that have been deeply explored by researchers due to their unique structure and reactivity^[1]

Benzonitrile occurs naturally in peanuts, hazelnuts, cocoa and dairy products, and has a wide range of applications in pharmaceuticals, agrochemicals, dyes and fine chemicals. For example, as a cyano source, it is used in the synthesis of drugs (such as anticancer drugs, antibiotics) and pesticides (such as insecticides, herbicides); It is used to prepare benzoic acid, aniline and other derivatives, and further synthesize dyes, fragrances and photosensitive materials; And because of the good solubility properties and stable physical properties of benzonitrile, it is often used as an important organic solvent. For example, Friedel-Crafts acylation and Grignard reagent reactions are especially suitable for systems that require high polarity and stability; as a reference or mobile phase additive in gas chromatography (GC) or high-performance liquid chromatography (HPLC), etc. There is a large market demand for benzonitrile compounds, and how to prepare benzonitrile compounds more efficiently has become an urgent problem.

The early production of benzonitrile was mainly obtained by extracting ammonium benzoate from coal tar or by dry distillation, but this method had a low yield and was not easy to collect. At present, the traditional industrial route of synthetic benzonitrile mainly relies on the cyanide method, the most well-known of which is the Sandmeyer cyanide method. Significant defects, such as the use of sodium cyanide or potassium cyanide, which are dangerous to operate; The generation of cyanide-containing wastewater is seriously polluted, the treatment cost is high, the need for strong acid or high temperature, high energy consumption and many side reactions, etc., so this method is gradually replaced by other production processes. In recent years, the synthesis strategy of directly preparing aromatic nitrile compounds by oxidative ammonia reaction using aromatic primary alcohols as raw materials has become a hot topic and frontier direction for many scholars due to its advantages of green efficiency, high atomic economy, etc^[6]. For example, benzyl alcohol is used as raw material to synthesize benzonitrile in one step through dehydroamination reaction, which has high green chemistry, high atomic economy and simplified process. The current research focuses on the development of high-efficiency

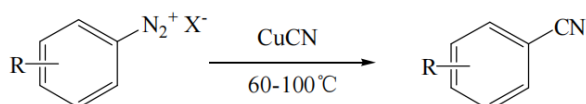
heterogeneous catalysts to solve the problem of dehydrogenation-ammonization synergy and selective control: due to the advantages of high specific surface area, adjustable active sites and good stability, supported metal catalysts (such as Cu/ γ - Al_2O_3) have become the key research direction to achieve efficient and environmentally friendly synthesis pathways due to the advantages of high specific surface area, adjustable active sites and good stability. Future research should focus on the development of high-performance non-precious metal catalysts, the optimization of the coupling process for reaction separation, and the large-scale engineering verification to promote the technology from the laboratory to the industrialization. This study is expected to provide a new strategy for the green synthesis of benzonitrile and promote the transformation of the fine chemical industry to an efficient and low-carbon direction.

1.1 Research progress on the synthesis of benzonitrile compounds

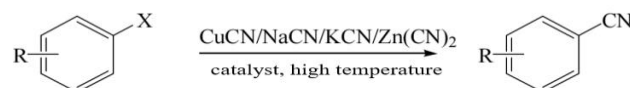
As the core intermediate of pharmaceuticals, pesticides and functional materials, the market demand for benzonitrile compounds continues to rise. In the early 19th century, the early production of benzonitrile was mainly obtained by extracting ammonium benzoate from coal tar or dry distillation, but the yield of the above methods was generally low, and the product separation was difficult, which was difficult to meet the needs of large-scale production. In order to meet the market demand, how to efficiently prepare benzonitrile compounds is the current research hotspot, and the following are the common preparation methods of benzonitrile:

(1) Halogenated aromatic hydrocarbon cyanidation method

The preparation of cyano compounds by halogen-cyano exchange reaction between halogenated benzene and cyano reagents has become a classic method for constructing cyano structures in the field of organic synthesis. The most well-known of these is the Sandmeyer cyanide method^[10]



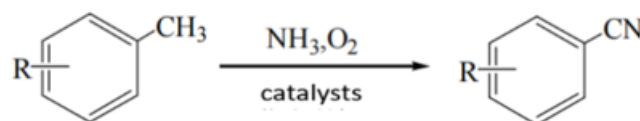
For the cyanide reaction of halogenated aromatic hydrocarbons, the researchers systematically explored the catalytic performance and reaction mechanism of metal cyanide. Mowry^[11] were the first to use CuCN as the cyano-based source to achieve efficient conversion of Bromo aromatic hydrocarbons in heterogeneous systems. Cassar^[12] and Takagi^[13] further extended to the NaCN/KCN system, and found that alkali metal cyanide could increase the reactivity of chlorinated aromatic hydrocarbons, but it needed to be driven by high temperatures above 200 °C. The Maligers team^[14] innovatively introduced $\text{Zn}(\text{CN})_2$ as a bifunctional reagent, and its cyano release was synchronized with halogen capture, reducing the formation of by-products.



However, the above methods rely on highly toxic cyanide and have high energy consumption, which does not meet the requirements of modern industrial green production and environmental protection, prompting follow-up research to turn to the development of low-toxicity complexes and green catalytic systems.

Schareina et al.^[15] based on $\text{K}_4\text{Fe}(\text{CN})_6$, which can achieve efficient conversion of Bromo aromatic hydrocarbons at a temperature of 120 °C with $\text{Pd}(\text{OAc})_2/\text{dppf}$ as the catalytic center and N-methyl pyrrolidone as the solvent. The reactivity is high, and it can react with halogenated aromatic hydrocarbons, which not only has an ideal yield, is easy to treat after the reaction, but also does not cause pollution to the environment.

(2) Toluene "gas-phase ammonia oxidation" method



Gas-phase ammonia oxidation based on toluene and its derivatives^[16] is one of the representative pathways for the green synthesis of benzonitrile. The process uses toluene NH_3 and O_2 as raw materials, under the action of catalysts, through a fixed-bed reactor to achieve continuous production, the method adopts atmospheric pressure operation, the reaction temperature is moderate, no special solvent is used, and no pollutant emission is required.

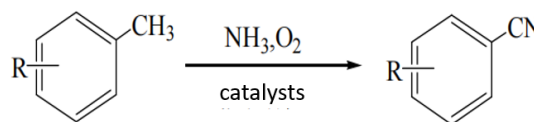
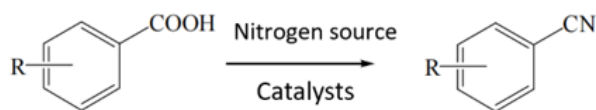
(3) Aniline compounds



Xu Yang's team^[19] reported a process route for the synthesis of o-methyl nitrile using o-methylaniline as raw material, in which o-methylaniline was diazotized in an acidic medium to prepare o-methylbenzene diazo salt, and then the diazo group was converted to cyano with the help of a copper salt catalytic system, which could efficiently synthesize o-methyl benzonitrile.

This method continues the limitations of the traditional diazonium salt substitution reaction cyanide use, and still needs to use toxic cyanide, which has problems such as high toxicity of raw materials and complex process operation. However, the recycling technology for the preparation of cuprous cyanide from cyanide-containing wastewater was established^[20]^[19-20], which realized the recycling of cyanide ions and reduced the consumption of total cyanide in the system, showing a good industrial prospect in wastewater treatment.

(4) Benzoic acid compounds



The reaction of benzoic acid compounds and urea to prepare benzonitrile compounds is a classic synthesis path that has attracted much attention. Taking the [22] Chen Hua's team [21] as an example, o-toluidate and urea are directly mixed and melted to obtain o-toluamide intermediates, and then phthalonitrile is obtained by dehydration, and the total yield of the reaction can reach 94.5%. In this system, urea has a dual role, providing nitrogen to the cyano group and acting as a fluxing agent. This synthesis method has the advantages of simple operation process, easy access to raw materials, and high yield, but it also has significant drawbacks: if the temperature is not properly controlled, urea is easy to decompose and polymerize, and the sublimation of o-toluic acid is more serious, which is easy to cause pipeline blockage.

In view of the above defects, Yi Bing [23] using diphenyl ether as solvent and p-toluic acid and urea as raw materials. This method has a smoother reaction, higher product purity, and improved process conditions, which provides a better solution for the large-scale production of benzonitrile compounds.

(5) Benzoaldehyde compounds

When benzofunrile compounds are synthesized from benzaldehyde compounds as starting materials, they can be divided into one-step method and two-step method according to the different reaction pathways.

Zong Zhengang et al [24] Synthesized p-hydroxy benzonitrile in one step with p-hydroxybenzaldehyde. Under the condition of heating and reflux, p-hydroxybenzaldehyde, hydroxylamine hydrochloride and anhydrous formic acid were reacted in one pot, and the yield of the target product benzonitrile was 98%. The one-step synthesis process has a simple reaction path and high product yield. However, the system relies on anhydrous formic acid as a solvent, which is highly corrosive and easy to release irritating gases, making it difficult to break through the bottleneck of industrial production.

Song Bin's team [25] proposed a two-step synthesis method of p-methoxy benzonitrile, in which p-methoxy benzaldehyde was used as an organic solvent and reacted with hydroxylamine salt to form the intermediate p-methoxy benzaldehyde oxime under mild conditions. Under the action of acetic anhydride or phosphoric anhydride dehydrator, the oxime group is converted into cyano group, and the total yield can reach more than 80%. Compared with the limitations of the one-step process, which relies on corrosive media, the oxime and dehydrating agents used in this process are not only inexpensive and easy to obtain, but also can be carried out under mild conditions, with simple equipment and easy operation, which is very suitable for the needs of industrial production, despite the increase in the number of two-step reaction steps.

(6) Benzyl alcohol compounds

In recent years, the synthesis strategy of directly preparing aromatic nitrile compounds by oxidative ammonia reaction using aromatic primary alcohols as raw materials has become a hot spot and frontier direction of many scholars due to its advantages of green efficiency and high atomic economy, forming a technical pattern of parallel development of heterogeneous catalytic systems.

Mizuno's team [26] used $\text{Ru}(\text{OH})_x/\text{Al}_2\text{O}_3$ and $\text{Ru}(\text{OH})_x/\text{TiO}_2$ bifunctional catalysts to achieve the dehydrogenation and ammoniation of benzyl alcohol and its derivatives in an oxygen atmosphere, and the conversion rate of benzyl alcohol and its derivatives could reach 92-95% and the selectivity of nitriles to more than 88% by regulating the degree of hydroxylation of Ru species. The system integrates the dehydrogenation active site (metal Ru) and ammonia activation site (acid support) at the nanoscale, which provides a theoretical model for the subsequent design of noble metal catalytic system.

Yadav et al. [27] focused on non-precious metal catalytic systems, using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as catalysts, using the dual functions of ammonium formate: it not only participates in the construction of C-N bonds as a nitrogen source, but also promotes the redox of $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ produced by pyrolysis. At 120 °C at atmospheric pressure, benzyl alcohol can be converted into corresponding nitrile compounds, a strategy that combines cheap metal catalysts with green oxidants (air) and solid nitrogen sources, opening up a new path for industrial-scale arnile production.

1.2 Research progress on ammonia oxidation reaction of benzyl alcohol

The core driving force for the preparation of benzonitrile lies in the rigid demand for benzonitrile in pharmaceutical, material, new energy and other industries. Green synthesis technology breaks through the bottleneck of traditional processes; Global environmental protection regulations and carbon neutrality goals have forced industrial upgrading. Therefore, the development of efficient and low-cost benzonitrile synthesis process is not only a hot spot in academic research, but also an inevitable choice for the sustainable development of the chemical industry. Catalytic dehydroammoniation of benzyl alcohol to prepare benzonitrile is one of the research hotspots in the field of green chemistry in recent years. At present, domestic research focuses on the development of non-noble metal catalysts, the analysis of reaction mechanisms and the optimization of process integration, and has made breakthroughs in industrial application potential. Foreign research is dominated by the design of precious metal catalysts and multi-scale mechanism research, focusing on the combination of basic science and industrialization. At present, the development trend at home and abroad is as follows:

1.2.1 Monometallic catalysts

(1) Copper-based catalysts

Cu/ZrO₂-Al₂O₃ dual carrier catalyst can better disperse the active component Cu by adjusting the Cu⁺/Cu⁰ ratio through ZrO₂, and using the good mechanical strength and large specific surface area of Al₂O₃. ZrO₂ has unique chemical properties and redox properties, and can interact with Cu to provide a suitable active environment for catalytic reactions. At 290 °C and NH₃/benzyl alcohol = 3:1, the conversion rate was 89 % and the selectivity was 93 %^[28]

The Cu/Y zeolite was prepared by loading copper species, combining the catalytic activity of copper and the structural and acidic advantages of Y-type zeolite, and inhibiting the side reactions at the same time, so as to achieve efficient synthesis of benzonitrile. At a reaction temperature of 310 °C, 87% selectivity for benzonitrile was obtained^[29]

The CuI/bipyridine/TEMPO system has certain advantages in the ammonia oxidation of benzyl alcohol to benzonitrile, ammonia water is used as the nitrogen source, the catalyst is prepared in the ratio of n(CuI):n(Bipy):n(TEMPO)=1:1:1, and the alcohol is catalytically oxidized to produce the corresponding nitrile by using a safe and reliable nitrox mixture (φ(O₂)=8%) as the terminal oxidant, and the reaction is carried out in an oxygen atmosphere for 8 hours at 120 °C. The conversion rate of benzyl alcohol was 99.3 %, and the selectivity of benzonitrile was 99.8% °C^[30]

(2) Cobalt-based catalysts

The Co/ZSM-5 catalyst uses the ion exchange method to load Co²⁺ onto the zeolite backbone, and uses the synergistic effect of the Co²⁺ site and the Brønsted acid site to activate benzyl alcohol to generate benzaldehyde intermediates. Promote the dissociation of NH₃ into NH₂^{*}, which is condensed with benzaldehyde to form imine; The ZSM-5 pore restricts the formation of macromolecular by-products. At a temperature of 280 °C, the feed ratio of benzyl alcohol to NH₃ was 1:4 (molar ratio), the benzyl alcohol conversion was 75 %, and the benzonitrile selectivity was 90 %^[31] These catalysts can reduce side reactions, improve the yield and quality of benzonitrile, and reduce energy consumption and equipment requirements.

In the supported Co₃O₄ catalyst, the strong oxidation of Co³⁺ can promote the activation of toluene methyl C-H bonds, and CeO₂ as a carrier has good surface alkalinity, which can enhance the adsorption of NH₃, so that NH₃ molecules can be enriched and activated on the surface of the catalyst, providing sufficient nitrogen source for ammonia oxidation reaction. The oxygen storage and oxygen release capacity of CeO₂ can regulate the concentration of oxygen species on the catalyst surface, which helps to maintain the activity and selectivity of the catalytic reaction. At 325 °C, the benzyl alcohol conversion rate was 45 %, and the benzonitrile selectivity was 83 %^[32]

(3) Platinum-based catalysts

Pt/TiO₂ single-atom catalyst, Pt is loaded on the TiO₂ support in the form of a single atom, maximizing the utilization of atoms, so that each Pt atom can participate in the reaction as an active center, and the oxygen vacancy on the surface of TiO₂ will change the electronic structure of the TiO₂

surface, making it have a higher electron cloud density and stronger adsorption capacity, and can form a strong interaction with Pt atoms, thereby improving the catalytic efficiency at 200 °C. The conversion rate of benzyl alcohol was 99 % and the selectivity of benzonitrile was 98 %^[33] but the cost was too high.

Pt/Al₂O₃ catalyst was prepared by impregnation method for the reaction of toluene ammonia oxidation to benzonitrile. In a fixed-bed reactor with toluene and ammonia as raw materials and air as the oxidant, it was found that when the Pt load was 1 % (mass fraction) and the reaction temperature was controlled at 280 °C, the conversion rate of toluene could reach 55 %, and the selectivity of benzonitrile was as high as 92 %^[34] The catalyst showed good stability in the reaction, and the catalytic activity did not decrease significantly after 100 hours of continuous reaction.

The highly dispersed Pt/Al₂O₃ catalyst was prepared by the improved deposition-precipitation method, and the Pt nanoparticles were highly dispersed on the surface of the Al₂O₃ support, which increased the active site and improved the efficiency of the catalytic reaction. In the reaction of ammonia oxidation of benzyl alcohol to benzonitrile, the reaction temperature was 250 °C, the pressure was atmospheric, and ammonia and benzyl alcohol were used as raw materials, and the catalyst showed good catalytic performance, with a conversion rate of 60 % for benzyl alcohol and a selectivity of 92 % for benzonitrile^[35]

1.2.2 Bimetallic catalysts

The California Institute of Technology (Caltech) has developed a Pd-Cu/HTs bimetallic catalyst with a synergistic effect between Pd and Cu. Pd has good adsorption and activation capacity, which plays a key role in the dehydrogenation process of benzyl alcohol. Cu plays a role in regulating the adsorption and conversion of reaction intermediates, changing the electronic structure and surface properties of Pd, so that the reaction of benzyl alcohol dehydroamination to benzonitrile after the combination of the two has better catalytic performance. The conversion rate of benzyl alcohol was 90 % and the selectivity of benzonitrile was 82 % at 180 °C^[36] It can reduce the energy consumption in the reaction process, and the high temperature resistance requirements of the reaction equipment are relatively low, reducing the equipment cost and operation risk.

In the Fe-Cu bimetallic catalyst, Fe-Cu bimetallic nanoparticles were loaded on nitrogen-doped mesoporous carbon (NC) by co-impregnation-hydrogen reduction method, and the Fe/Cu molar ratio was 1:2, and the Fe³⁺/Fe²⁺ redox cycle activated the C-H bond under the synergistic action of Fe and Cu. Cu⁺ promotes NH₃ dissociation to form NH₂^{*} intermediates; The conductivity of nitrogen-doped carbon accelerates electron transfer and inhibits carbon deposition. At a temperature of 200 °C and atmospheric pressure, the feed ratio of benzyl alcohol to NH₃ was 1:3 (molar ratio), the conversion rate of benzyl alcohol was 68 %, and the selectivity of benzonitrile was 75 %^[37] The raw material cost of Fe-Cu catalyst is much lower than that of Pd-based catalyst system. The reaction temperature is 30 °C lower than that of the traditional process (250-300 °C). Atmospheric operation is

compatible with carbon steel reactors and does not require superalloys.

Pt-Fe/Al₂O₃ catalyzed the preparation of benzonitrile. Fe promotes NH₃ dissociation and provides reactive nitrogen species for ammonia oxidation reactions. Ability to react more easily with toluene or its oxidation intermediates; Pt activates the methyl C-H bond, making the methyl group in the toluene molecule more prone to oxidation to form key intermediates, such as benzaldehyde or imine derivatives of benzyl alcohol, which are further converted to benzonitrile to promote the formation of benzonitrile. At 280 °C, the benzonitrile selectivity was 92 %, and the toluene conversion was 55 %^[38]

1.2.3 Research and development trend of ammonia oxidation reaction of benzyl alcohol

In addition to the existing bimetallic catalysts such as Pd-Cu and Pd-Au, more diverse metal alloys or composite catalysts should be developed to further optimize the catalytic performance, improve the conversion rate of benzyl alcohol and the selectivity of benzonitrile, and enhance the stability and anti-poisoning ability of the catalysts.

Single-atom catalysts have broad application potential in the synthesis of benzonitrile due to their unique active sites and plateau utilization. It is expected to achieve a breakthrough in the field of green synthesis of fine chemicals and promote the transformation of benzonitrile production to high efficiency, low consumption and environmental protection.

Novel carrier materials with special properties, such as those with high specific surface area, good electron conductivity, and unique pore structure, are searched to improve the performance of catalysts by dispersing active components. In addition, the effects of various additives on the performance of catalysts were studied, and the electronic structure and surface properties of catalysts were modified by adding appropriate additives to improve the catalytic activity, selectivity and stability.

We are committed to developing a catalytic system that can be carried out efficiently under lower temperature and milder reaction conditions, reducing the energy consumption of the reaction and the requirements for equipment. The use of green and environmentally friendly reaction media, such as ionic liquids, supercritical fluids, etc., replaces traditional organic solvents, reduces environmental pollution, and may improve the mass and heat transfer effects of the reaction, and improve the reaction efficiency and selectivity. Continuous and automated production: Develop continuous production processes to improve production efficiency and product quality stability, and reduce labor costs and long production cycles caused by intermittent operations. At the same time, the use of advanced automatic control technology to achieve accurate control of the reaction process, improve the safety and reliability of production. The benzyl alcohol dehydroamination reaction was integrated with the subsequent separation, purification and other processes to design a more efficient integrated production process.

With the help of computational chemistry methods such as density functional theory and molecular simulation techniques, the catalytic reaction mechanism and the structure-

performance relationship of catalysts are studied in depth, so as to provide theoretical guidance for the rational design and optimization of catalysts and accelerate the research and development process of new catalysts. In-situ characterization techniques such as in-situ infrared spectroscopy are used to monitor the structural changes of catalysts and the generation and transformation of reaction intermediates in real time during catalytic reactions, providing direct experimental evidence for revealing the reaction mechanism and optimizing catalysts.

1.3 The content and significance of the research project

1.3.1 The significance of the research project

Benzonitrile is a high value-added organic intermediate, which is an important raw material for pesticides, pharmaceuticals and polymer materials, and the market demand continues to grow. The efficient synthesis of benzonitrile can reduce the cost of downstream industries and enhance the competitiveness of the fine chemicals industry chain. Cyanide (such as NaCN, KCN) or nitrile reagents are often used in the traditional synthesis of benzonitrile, which has high operational risks. Serious pollution, high treatment cost, high energy consumption and many side reactions. Using benzyl alcohol and ammonia as raw materials, the reaction conditions are mild and in line with the principles of green chemistry. The reaction path is the direct dehydrogenation and condensation of benzyl alcohol and NH₃ to form benzonitrile, which has a high theoretical atomic utilization rate and reduces the waste of resources.

The price of the Cu-based catalyst used in this study is much lower than that of precious metals (such as Pd and Pt), and the γ -Al₂O₃ support is easy to prepare on a large scale, which is suitable for industrial production. Mild reaction conditions significantly reduce energy consumption and equipment requirements. The high selectivity of the catalyst for the product benzonitrile increases the yield of benzonitrile.

This study not only provides a new path for the green synthesis of benzonitrile, but also deepens the understanding of the active site, support effect and reaction kinetics of copper-based catalysts, and has significant environmental benefits (reducing the use of toxic reagents) and economic benefits (low cost and high selectivity). The results can be extended to the synthesis of other nitrile compounds, helping to upgrade the technology of the fine chemical and pharmaceutical industries.

1.3.2 The content of the research project

Research content: Supported metal catalysts (such as Cu/ γ -Al₂O₃) are an important breakthrough direction to solve the problem of dehydrogenation-ammonia synergy and selective control, catalyze the dehydroamination of benzyl alcohol to prepare benzonitrile, and realize green synthesis due to their high specific surface area, adjustable active sites and good stability.

II. EXPERIMENTAL PART

2.1 Experimental reagents and equipment

2.1.1 Experimental equipment

TABLE 2.1 The main instrument of the experiment

Instrument	Model	Manufacturer
Electronic balances	CP214	OHAUS Instruments (Shanghai) Co., Ltd
Magnetic stirrer instrument	HJ-4	Shanghai Shuaideng Instrument Co., Ltd
Circulating water type multi-purpose vacuum pump	Model	Manufacturer
Electric blast drying oven	SHB-III	Henan Yuhua Instrument Co., Ltd
Scanning electron microscope	DHG-9140	Shanghai Yiheng Scientific Instrument Co., Ltd
	Zeiss Supra55	ZEISS AG, Germany
Thermostatic bath	ISO9001	Ningbo Tianheng Instrument Factory
Tube furnaces	BTF-1200C	Beyke Equipment Technology GmbH
Gas chromatograph	7890 B	Agilent Technologies

2.1.2 Experimental reagents

TABLE 2.1.2 Experimental raw materials and manufacturers

Chemical	Factory
Al ₂ O ₃	Evonik Specialty Chemicals GmbH
Copper nitrate trihydrate (Cu(NO ₃) ₂ ·3H ₂ O)	Shanghai Titan Technology Co. Ltd
Ferric nitrate (Fe(NO ₃) ₃ ·9H ₂ O)	Shanghai Titan Technology Co. Ltd
Cobalt nitrate hexahydrate (Co(NO ₃) ₂ ·6H ₂ O)	Shanghai Titan Technology Co. Ltd
Zinc nitrate hexahydrate (Zn(NO ₃) ₂ ·6H ₂ O)	Shanghai Titan Technology Co. Ltd
Cerium nitrate hexahydrate (Ce(NO ₃) ₃ ·6H ₂ O)	Shanghai Titan Technology Co. Ltd
Absolute ethanol (C ₂ H ₆ O)	Sinopharm Chemical Reagent Co. Ltd
Ammonia (NH ₃)	Changzhou Wujin Huayang Gas Co. Ltd
Benzyl alcohol (C ₇ H ₈ O)	Anage Chemical
Dibenzene ether (C ₁₄ H ₁₀ O)	Shanghai Titan Technology Co. Ltd
Benzoaldehyde (C ₇ H ₆ O)	Shanghai Aladdin Biotechnology Co. Ltd
Benzamine (C ₇ H ₉ N)	Shanghai Aladdin Biotechnology Co. Ltd
Cyclohexane (C ₆ H ₁₂)	Shanghai Titan Technology Co. Ltd
Distilled water (H ₂ O)	Changzhou University

2.3 Catalyst characterization

2.3.1 X-ray powder diffraction (XRD)

The sample phase was determined by using RIGAKU Corporation SmartLab X-ray diffractometer, using a Cu-K α ray source ($\lambda=1.54 \text{ \AA}$), with a graphite monochromator, setting current of 40 mA, tube pressure of 40 kV, scanning angle in the range of 5~50°, and scanning rate controlled at 5°/min.

2.3.2 N₂ -physical adsorption-desorption

The samples were degassed at 200 °C for 8 h at 200 °C to remove impurities and adsorbents on the surface and pores of the samples. The adsorption desorption and desorption characterization was performed at -196 °C in the environment of liquid nitrogen, and the N₂ physisorption-desorption isotherm was obtained.

2.3.3 Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) was used to characterize the microscopic morphology and surface structure of the samples. The scanning electron microscope used to determine the topography of the sample was from Zeiss Supra55 from Zeiss in Germany, EHD=5.0 kV, WD=6.9 mm.

2.3.4 Infrared absorption spectroscopy

The acidity of the support and catalyst (Bronsted/Lewis) was studied by pyridine adsorption infrared spectroscopy (Py-IR). The test uses pyridine as the probe molecule and the

sample is characterized by an infrared spectrometer from Bruker with the model TENSOR 27 spectrometer. The specific steps are as follows: first, make a self-loading tablet of 20 mg of sample; Place the treated lamellae in an in-situ cell and vacuum process at 400 °C for approximately 2 h. Wait for cooling to room temperature before collecting the background spectrum. The pyridine was then blown into the reaction cell with a stream of 10 mL/min N₂ gas and held for approximately 20 minutes. The temperature was then raised to 150 °C for 20 min, and the Py-IR spectra were collected by subtracting the background spectrum of the sample.

2.3.5 NH₃ - Programmed Temperature Reduction

NH₃-TPD characterization was performed using a Micromeritics AutoChem ASAP 2920 instrument. Firstly, the prepared 100 mg sample to be tested was loaded into a quartz reaction tube, heated to 550 °C, purged and pretreated with the He gas flow for 2 h to remove the surface physisorption substances, and after the sample was cooled to 120 °C, NH₃-He mixed gas (10vol% NH₃) was introduced into the sample for 30 minutes. This temperature was then maintained and the gas mixture was switched to a stream of He gas for 2 h to remove residual physisorption NH₃ from the sample surface. Finally, the sample was placed in a He atmosphere, heated from 120 °C to 600 °C at a heating rate of 10 °C/min, and the desorption signal was measured by a thermal conductivity detector (TCD).

2.3.6 H₂-programmed temperature reduction

Temperature-programmed reduction experiments were performed on a Micromeritics AutoChem ASAP 2920 instrument equipped with a Thermal Conductivity Detector (TCD). First, the sample to be tested is calcined in a muffle furnace to remove the influence of moisture and impurities contained in the sample. Subsequently, 50 mg of calcined samples were weighed and loaded into quartz reaction tubes, and the samples were raised from room temperature to 700 °C at a heating rate of 10 °C/min in an H₂-Ar (10 vol% H₂) mixture atmosphere, and H₂ consumption was recorded using a TCD detector during the experiment.

2.4 Catalyst preparation

Cu/ γ -Al₂O₃ with 5wt% copper loading was prepared by wet impregnation method. SB powder purchased from Evonik Specialty Chemicals GmbH was used as a carrier. Firstly, the SB powder was dried at 80 °C for 6~12 hours, calcined at 550 °C for 4 h to obtain γ -Al₂O₃, ground and sieved for later use. 0.94 g of copper nitrate trihydrate (Cu (NO₃)₂·3H₂O) was weighed and stirred magnetically for 30 min until it was completely dissolved in 50 mL of absolute ethanol. 5.0 g of SB powder (γ -Al₂O₃ carrier) was placed in a round-bottom flask, copper nitrate ethanol solution was added dropwise, and ultrasonically dispersed in a constant temperature water bath at 30 °C was stirred until the ethanol was completely volatilized. After immersion, the samples were heat-treated and dried overnight in a 100 °C electric blast drying oven, followed by calcination in a tube furnace at 500 °C for 5 h. Cu/ γ -Al₂O₃ powder obtained. The tablets were pressed at a pressure of 6 MPa in the tablet press, and after crushing, the 40-60 mesh particles were collected by a standard screen

classification, and finally the Cu/ γ -Al₂O₃ particles were dried and stored for later use.

Fe/ γ -Al₂O₃ catalyst Co/ γ -Al₂O₃ catalyst Fe-Cu/ γ -Al₂O₃ catalyst Cu-Zn/ γ -Al₂O₃ catalyst Cu-Co/ γ -Al₂O₃ catalyst Cu-Ce/ γ -Al₂O₃ the preparation method of the catalyst is the same as that described above.

2.5 Catalyst activity test

In this study, a fixed-bed reactor was used to evaluate the performance of benzyl alcohol ammonia oxidation reaction. The experimental apparatus is composed of a quartz tube with an inner diameter of 6.0 mm and a length of 600 mm, in which the Cu/ γ -Al₂O₃ catalyst is mixed with silicon carbide and filled in the constant temperature section, and the effective height of the catalytic bed is 150 mm (the actual loading capacity of the catalyst is 2.0 g). The temperature of the reaction system was maintained at 350 °C, and the ammonia carrier gas flow rate was controlled at 22 mL/min (standard state).

The reaction raw material was a prepared benzyl alcohol/cyclohexane mixture solution (20% benzyl alcohol by mass), and the liquid phase was continuously injected by a microflow syringe pump. The liquid phase product was collected every 30 minutes and quantified by an Agilent 7890B gas chromatograph. The conversion rate and selectivity are calculated as follows:

$$X = \frac{n_0 - n_1}{n_0} \times 100\% \quad (1)$$

$$S_i = \frac{n_i}{n_0 - n_1} \times 100\% \quad (2)$$

X is the conversion rate of benzyl alcohol, Si is the selectivity of benzonitrile, n₀ is the initial molar fraction of benzyl alcohol, n₁ is the molar fraction of unreacted benzyl alcohol, and ni is the molar fraction of benzonitrile.

III. RESULTS & DISCUSSION

3.1 Screening of benzyl alcohol dehydroamination reaction conditions

3.1.1 Metal loading screening

The dehydroamination of benzyl alcohol to benzonitrile is an important organic synthesis reaction, and the core challenge lies in the design of the catalyst: it is necessary to achieve both high dehydrogenation activity (conversion of benzyl alcohol to benzaldehyde) and efficient ammoniation capacity (benzaldehyde and NH₃ to benzonitrile). By reviewing the relevant literature at home and abroad, in the study of the use of catalyst benzyl alcohol dehydroamination to prepare benzonitrile, the common catalyst systems include:

copper-based catalysts, platinum-based catalysts, cobalt-based catalysts, etc., and the partially supported catalysts such as copper-based, cobalt-based and bimetallic catalysts were selected for preparation and their selectivity and conversion rate in catalyzing the preparation of benzyl alcohol to benzonitrile, and the optimal supported metals were screened.

TABLE 3.1 shows the conversion and selectivity of different catalysts under the same catalytic conditions. Reaction conditions: atmospheric pressure, 2 g catalyst, 20 wt% benzyl alcohol cyclohexane solution, reaction temperature at 350 °C; The reaction was performed in a fixed-bed reactor and the data were analyzed by GC and GC-MS.

TABLE 3.1 Comparison of selectivity and conversion rate of various supported catalysts

Catalyst	Conv. (%)	Selectivity (%)							
		1	2	3	4	5	6	7	8
Fe/C-Al ₂ O ₃	99	22.1	\	11.8	30.7	\	20.1	9.0	3.2
Cu/ γ -Al ₂ O ₃	100	11.1	\	88.9	\	\	\	\	\
Co/C-Al ₂ O ₃	100	8.7	\	20.1	44.8	\	19.6	4.8	0.9
Fe-Cu/ γ -Al ₂ O ₃	100	17.7	\	15.7	28.6	\	21.1	10.8	2.3
Cu-Zn/ γ -Al ₂ O ₃	100	3.6	0.3	13.2	17.9	\	23.0	35.0	4.5
Cu-Co/ γ -Al ₂ O ₃	100	13.5	\	14.9	33.8	\	23.3	8.5	2.2
Cu-Ce/ γ -Al ₂ O ₃	100	9.8	\	60.8	12.1	\	7.2	2.1	7.2

Description: 1. Toluene, 2. Benformaldehyde, 3. Benzonitrile, 4. Benylamine, 5. Dibenzyl ether, 6. Dibenzylamine, 7. N-Bentenbutylamine, 8. Others

By comparing multiple catalysts to catalyze the same mass of benzyl alcohol under the same conditions, it can be seen from the gas chromatography results that the conversion rate of all catalysts is close to or reaches 100% (only Fe/ γ -Al₂O₃ is 99%), and the catalysts show extremely high catalytic activity at 350 °C and atmospheric pressure, and the benzyl alcohol conversion ability is excellent.

The selectivity of the Cu/ γ -Al₂O₃ catalyst for benzonitrile was as high as 88.9 %, which was significantly higher than that of other catalysts, and the benzonitrile could be prepared with high selectivity, while the other products were almost not generated, and the reaction path was highly specific. The monometallic Cu was selected as the load metal.

3.1.2 Vector optimization

Table 3.2 shows the conversion and selectivity of the catalyst by supporting Cu on different supports under the same conditions. Reaction conditions: atmospheric pressure, 2 g catalyst, 20 wt% benzyl alcohol cyclohexane solution, reaction temperature at 350 °C; The reaction was performed in a fixed-bed reactor and the data were analyzed by GC and GC-MS.

TABLE 3.2 Conversion and selectivity of catalyst reactions with different supports

Entry	Catalyst	Temp. (°C)	Ammonia (mL/min)	Conv. (%)	Selectivity (%)						
					1	2	3	4	5	6	7
1	/	350	22	100.0	43.4	\	3.6	45.3	\	\	5.0
2	SiO ₂	350	22	100.0	49.5	\	1.7	42.8	0.5	5.5	\
3	γ -Al ₂ O ₃	350	22	100.0	29.5	\	5.7	13.6	15.0	29.1	7.0
4	Cu/SiO ₂	350	22	100.0	2.5	\	33.5	19.7	17.6	22.4	4.1
5	Cu/ γ -Al ₂ O ₃	350	22	100.0	11.1	\	88.9	\	\	\	\

Instructions: 1. Toluene, 2. Benzoaldehyde, 3. Benzonitrile, 4. Benylamine, 5. Dibenzylamine, 6. N-benzenebutylamine, 7. other

Under the conditions of reaction temperature of 350 °C and ammonia gas flow rate of 22 mL/min, according to the

conditions of no catalyst, pure support SiO₂, pure support γ -Al₂O₃, Cu/SiO₂ catalyst and Cu/ γ -Al₂O₃ catalyst, The

conversion rate and selectivity obtained by the reaction were 100.0 %, and the data showed that the product distribution was dispersed without catalyst or only with support (SiO_2 , $\gamma\text{-Al}_2\text{O}_3$), which proved that the active site of Cu metal was indispensable for directional catalysis. The selectivity of Cu/ $\gamma\text{-Al}_2\text{O}_3$ for benzonitrile was 88.9 %, which was significantly better than that of Cu/ SiO_2 , indicating that the adsorption and reaction path of the intermediates were optimized by surface acidity of the $\gamma\text{-Al}_2\text{O}_3$ support. Finally, the catalyst Cu/ $\gamma\text{-Al}_2\text{O}_3$ was selected.

3.1.3 Optimization of reaction conditions

Table 3.3 compares the conversion and selectivity of the reaction at different temperatures and different ammonia flow rates under the same conditions. Reaction conditions: atmospheric pressure, 2 g catalyst, 20 wt% benzyl alcohol cyclohexane solution, reaction temperature 350 °C, the

reaction was carried out in a fixed-bed reactor; Data were analyzed by GC and GC-MS.

As can be seen from Table 3.3, the selectivity of the target product benzonitrile increased from 56.4% to 88.9% with the increase of temperature, indicating that the high temperature (350 °C) promoted the dehydrogenation-ammoniation tandem reaction and inhibited the formation of side reactions. When the ammonia flow rate increased from 22 mL/min to 66 mL/min, the selectivity of benzonitrile decreased slightly from 88.9 % to 88.1 %, indicating that the low ammonia flow rate had met the reaction requirements and did not require excessive consumption.

Optimal conditions: Cu/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, 350 °C, ammonia flow rate 22 mL/min, benzyl alcohol conversion at this time, benzonitrile selectivity of 88.9 %, and few by-products. The system is both efficient and economical, and is suitable for industrial production.

TABLE 3.3 Conversion and selectivity of different reaction temperatures and ammonia flow rates

Entry	Catalyst	Temp. (°C)	Ammonia (mL/min)	Conv. (%)	Selectivity (%)						
					1	2	3	4	5	6	7
1	Cu/ $\gamma\text{-Al}_2\text{O}_3$	250	22	100.0	4.4	\	56.4	25.1	8.7	4.1	0.6
2	Cu/ $\gamma\text{-Al}_2\text{O}_3$	300	22	100.0	5.6	\	76.0	9.4	2.0	6.0	2.3
3	Cu/ $\gamma\text{-Al}_2\text{O}_3$	350	22	100.0	11.1	\	88.9	\	\	\	\
4	Cu/ $\gamma\text{-Al}_2\text{O}_3$	350	66	100.0	11.9	\	88.1	\	\	\	\

Instructions: 1.Toluene, 2.Benzaldehyde, 3. Benzonitrile, 4.Benzylamine, 5.Dibenzylamine, 6.N-benzenebutylamine, 7. other

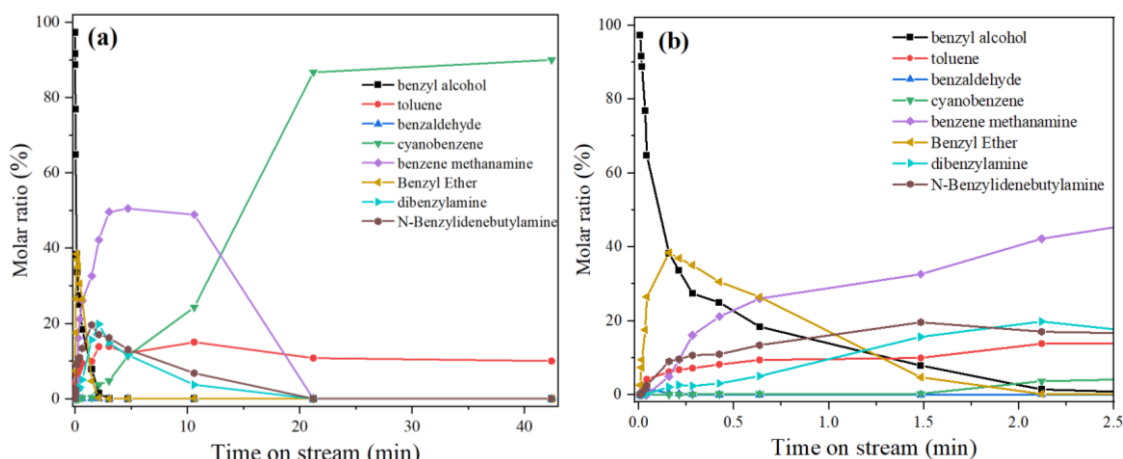


Figure 31 Concentration distribution curves of each substance under different reaction times

3.2 Reaction mechanism speculation

[39], the reaction intermediate and product concentration changes were analyzed by gas chromatography-mass spectrometry. The results showed that in addition to the main product benzonitrile, there was a small amount of toluene in the product, and the intermediate products mainly included benzaldehyde, benzylamine, dibenzyl ether, dibenzylamine, N-benzenebutylamine, etc. With the change of reaction time, the path of the reaction is estimated according to the change in the concentration of each substance.

As can be seen from Figure 31(a), the concentration curves of dibenzylamine and N-benzenemine increased within 0~3 min, and benzylamine concentration curve slowed down, and it was speculated that benzylamine may be condensed to form

N-benzenemine, and N-benzylene to form dibenzylamine by hydrogenation.

The curves of dibenzylamine and N-benzenemine decreased at 3~5 min, the concentrations of benzylamine increased slowly, the curves of dibenzylamine and N-benzenebutylamine continued to decrease at 3~5 min, the concentrations of benzylamine decreased slowly, and the concentrations of toluene and benzonitrile continued to increase. Later, the generation and disappearance of benzimine characteristic absorption peaks were observed in infrared spectrometry, and it was speculated that N-benzenemine was decomposed into toluene and benzonitrile, N-benzenemine was hydrogenated to benzimine, and dibenzylamine was decomposed into toluene and aniformalamine. In 11~22 min, the concentration of benzylamine decreased rapidly, the concentration of benzonitrile increased rapidly, and the curves

of dibenzylamine and N-benzenemine slowly decreased to disappear, and it was speculated that N-benzenemine was decomposed into toluene and benzonitrile, and benzoamine finally generated benzonitrile from three pathways.

The complexity of the reaction path is reflected in the dynamic competition between the main reaction (dehydrogenation → ammoniation → dehydration) and the side reactions, and benzaldehyde is a key intermediate and a necessary step of the main reaction.

As Figure 31 from Figure 3.1(b), the sudden decrease in benzyl alcohol concentration is synchronized with the rapid increase of benzyl ether concentration, the benzaldehyde concentration increases, and benzyl alcohol generates the key intermediate benzyl ether and a small amount of benzaldehyde at the Cu active site, and this process is carried out rapidly within 0~0.2 min, and it is speculated that a large amount of benzyl alcohol is self-condensed to form benzyl ether, and a small part of benzyl alcohol is dehydrogenated to form benzaldehyde. Subsequently, the concentration of benzyl ether decreased rapidly, the concentration of benzyl alcohol decreased slowly, the concentration of benzylamine increased, and the concentration of toluene increased slowly.

Subsequently, the concentration of benzaldehyde decreased rapidly, the benzonitrile curve slowly increased, and the concentration curve of N-benzenebutylamine increased slowly, and then the generation and disappearance of benzimine characteristic absorption peaks were observed in the infrared spectrometer, which was inferred to form benzimine with NH_3 , followed by the addition of part of benzimine to form benzamide, part of the benzimine dehydrogenation to form benzonitrile, and part of the benzimine deamination combined with benzamine to form N-Bententhotriline.

In order to verify the change pathways of each intermediate product in the speculation, Table 3.4 shows the conversion rate and selectivity of each product obtained by using benzyl ether, benzaldehyde, benzylamine and N-benzylbutamine as reactants to participate in ammonia oxidation reaction. The reaction conditions were atmospheric pressure, 350 °C, ammonia flow rate of 22 mL/min, 2 g catalyst, 20 wt% reactant cyclohexane solution, and the data were obtained by GC analysis. ^a The amount of catalyst is 50 mg.

TABLE 3.4 Conversion and selectivity of ammonia oxidation reaction of each reactant

Entry	Reactant	Ammonia (mL/min)	Conv. (%)	Selectivity (%)							
				1	2	3	4	5	6	7	8
1	Benzyl Ether	22	5.3	39.6	26.4	/	/	26.4	/	1.9	5.7
2	Benzyl Ether	22	12.6	35.7	9.5	/	/	8.7	1.6	21.4	3.2
3	Benzyl Ether	22	95.8	15.8	/	2.2	18.4	0.2	31.0	30.5	1.6
4	Benzyl Ether	22	100.0	21.2	/	75.2	/	/	/	/	2.3
5	Benzaldehyde	22	100.0	3.7	/	96.3	/	/	/	/	/
6	Benzylmethy lamine ^a	22	61.6	5.9	/	16.0	/	11.1	32.1	45.2	0.8
7	Benzylmethy Larry	22	100.0	9.0	/	91.0	/	/	/	/	/
8	N-Benzylidene benzylamine	22	100.0	5.2	/	94.8	/	/	/	/	/

Instructions: 1. Toluene, 2. benzaldehyde, 3. benzonitrile, 4. Benzylamine, 5. Benzyl alcohol, 6. Dibenzylamine, 7. N-benzenemine, 8. other

According to the relevant literature, the hydrogenation of the Cu site and the decomposition of benzyl ether into benzyl alcohol and toluene can be obtained from benzyl ether, and with the increase of conversion rate, benzyl alcohol and benzaldehyde disappear, and the path speculation is reasonable.

Serial number 6~7 shows that with benzamine as the reactant, under the condition of a small amount of catalyst, the selectivity of dibenzylamine and N-benzenemine is higher, check the relevant literature, benzamine and benzaldehyde condense to form dibenzylamine, Cu site dominates the dehydrogenation/hydrogenation process, and the acidic site of $\gamma\text{-Al}_2\text{O}_3$ promotes the dehydration and condensation steps, and benzamine is dehydrogenated under the action of catalyst to form benzonitrile, The addition of hydrogen and N-benzenemine to dibenzylamine is reasonable. Serial number 8 shows that N-benzene butylamine generates benzonitrile and a small amount of toluene at high conversion rate, and the path speculation is reasonable.

Figure 3.2 Diagram of possible reaction pathways of ammonia oxidation of benzyl alcohol below shows the estimated ammonia oxidation pathway of benzyl alcohol. Part of the benzyl alcohol is directly dehydrogenated to form benzaldehyde, and part of the benzyl alcohol is dehydrated and condensed to form dimethyl ether; Part of the dimethyl ether will be hydrogenated and re-decomposed into benzyl alcohol and toluene, and part of the dimethyl ether will be directly decomposed into benzaldehyde and toluene; Benzaldehyde dehydration and ammonia reaction to form unstable benzimine; Some animalides will be directly dehydrogenated to form benzonitrile, benzimine and benzamine can be converted to each other through dehydrogenation/hydrogenation, and some will remove ammonia and benzamine to form N-benzenbutylamine; Benzamine can be dehydrated and reacted with benzaldehyde to form N-benzenemine, which is converted to dibenzylamine through hydrogenation/dehydrogenation. N-benzenebutylamine removes toluene to form benzonitrile.

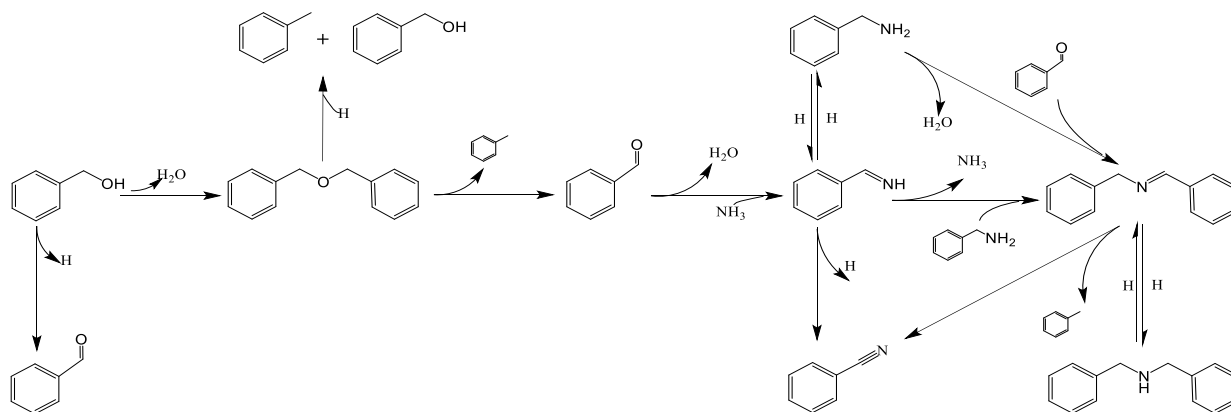


Figure 3.2 Diagram of possible reaction pathways of ammonia oxidation of benzyl alcohol

3.3 Characterization of Cu/ γ -Al₂O₃ catalyst

In order to comprehensively explore the physical and chemical properties of Cu/ γ -Al₂O₃ catalysts, this chapter comprehensively uses a variety of characterization methods: scanning electron microscopy (SEM) to observe its microscopic morphology, X-ray powder diffraction (XRD) to analyze the crystal structure, pyridine infrared spectroscopy to study the surface acidic sites, N₂ physisorption desorption test to obtain pore structure information, NH₃-TPD, H₂-TPD

technology explores the acidic strength of the surface and the characteristics of the active site of the metal.

According to Figure 3.33 most of the γ -Al₂O₃ particles are 5~20 μ m in size, with rough surface and well-developed pores. After Cu loading, the morphology of the active metal Cu was not damaged, and the metal Cu particles were dispersed on the surface of the support in the Cu/ γ -Al₂O₃ sample, which did not significantly damage the integrity of the original skeleton and increased the surface roughness.

3.3.1 Scanning electron microscope (SEM)

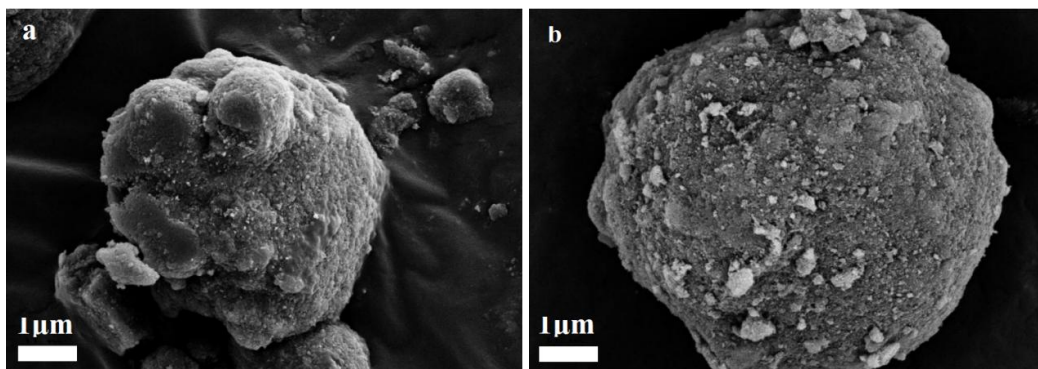


Figure 3.33 SEM images of 3(a) γ -Al₂O₃ and (b) Cu/ γ -Al₂O₃

3.3.2 X-ray powder diffraction (XRD)

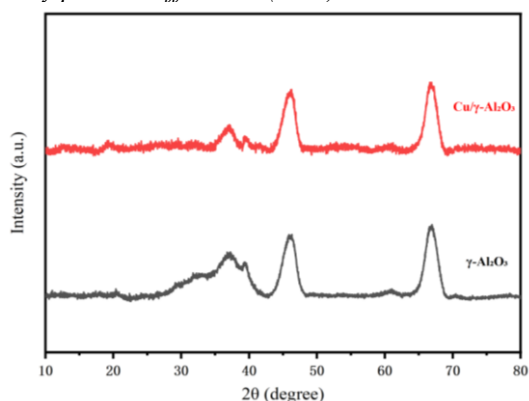


Figure 3.4 XRD plots of γ -Al₂O₃ and Cu/ γ -Al₂O₃

Figure 3.4 shows the XRD plots of γ -Al₂O₃ and Cu/ γ -Al₂O₃. As can be seen from the figures, both γ -Al₂O₃ and Cu/ γ -Al₂O₃ have their own typical diffraction characteristic peaks. γ -Al₂O₃ at 37.6°, 39.5°, 45.8°, 66.9°. The

characteristic peaks can correspond to the [222], [311], [400], and [440] crystal planes, respectively. and no other alumina phase characteristic peaks appear, and the support structure is stable. The diffraction absorption peak of Cu/ γ -Al₂O₃ is almost the same as that of γ -Al₂O₃, and there is no characteristic diffraction peak of Cu, indicating that Cu is highly dispersed in the carrier γ -Al₂O₃, and the number of effective active sites of Cu is large, and the catalytic efficiency is high.

3.3.3 NH₃-TPD test

Figure 3. shows the NH₃-TPD test plots of γ -Al₂O₃ and Cu/ γ -Al₂O₃ materials. Less than 300 °C is the weak acid area, and more than 300 °C is the strong acid area. It can be seen from the figure that the acidic strength of γ -Al₂O₃ is different from that of Cu/ γ -Al₂O₃, γ -Al₂O₃ has a Lewis acid site of 227 °C, and Cu/ γ -Al₂O₃ has a strong acid site of 397 °C in addition to the Lewis acid site at 227 °C due to the introduction of Cu, but according to the pyridine infrared map Cu/ There is no Bronsted acid on γ -Al₂O₃, so the introduction of Cu adds a

strong Lewis acidic site to $\gamma\text{-Al}_2\text{O}_3$, which makes $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ more acidic.

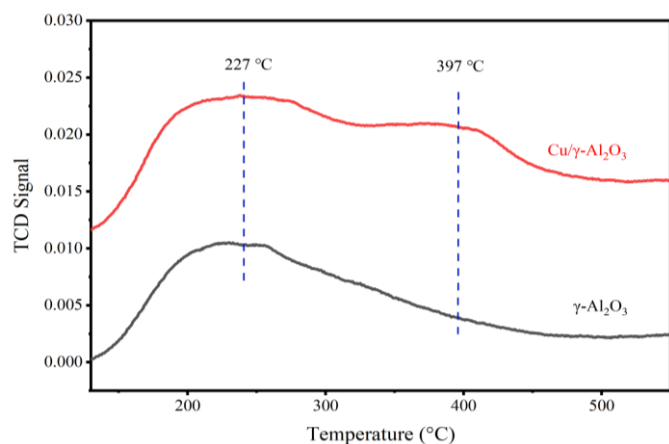


Figure 3.5 NH_3 -TPD test charts of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$

3.3.4 Pyridine infrared

Figure 3.shows the pyridine infrared pattern of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$. An absorption band at approximately 1450 cm^{-1} was observed in the $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ samples, which was related to the interaction of Py molecule with the Lewis acid site (L). The adsorption of surface acidity Py on the Lewis acid site of alumina results in the formation of a coordination-bonded Py, resulting in an absorption band of around 1490 cm^{-1} . The pair of bands observed at 1450 cm^{-1} can be classified as Py adsorbed on a tricoordinated Al^{3+} cation (tetrahedral Al cation with coordination unsaturation), which represents the strongest acidic Lewis site in alumina. There is no Bronsted acid with an absorption band of 1540 cm^{-1} on $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$.

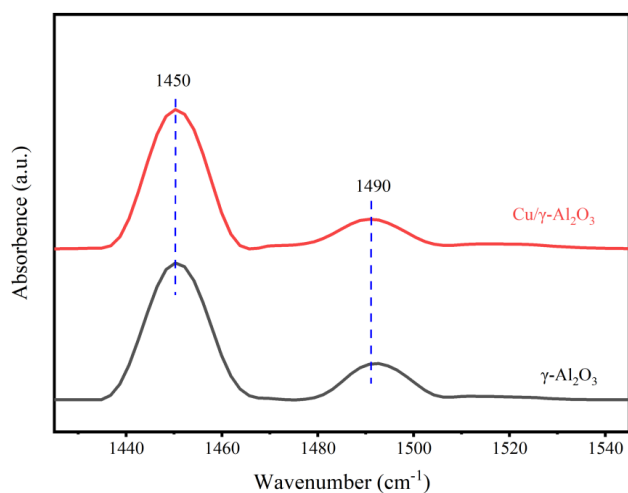


Figure 3.6 Pyridine infrared images of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$

Figure 3.shows the pyridine infrared pattern of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$. An absorption band at approximately 1450 cm^{-1} was observed in the $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ samples, which was related to the interaction of Py molecule with the Lewis acid site (L). The adsorption of surface acidity Py on the Lewis acid site of alumina results in the formation of a coordination-bonded Py, resulting in an absorption band of around 1490 cm^{-1} . The pair of bands observed at 1450 cm^{-1} can be classified as Py adsorbed on a tricoordinated Al^{3+}

cation (tetrahedral Al cation with coordination unsaturation), which represents the strongest acidic Lewis site in alumina. There is no Bronsted acid with an absorption band of 1540 cm^{-1} on $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$.

3.3.5 N_2 -physical adsorption and desorption

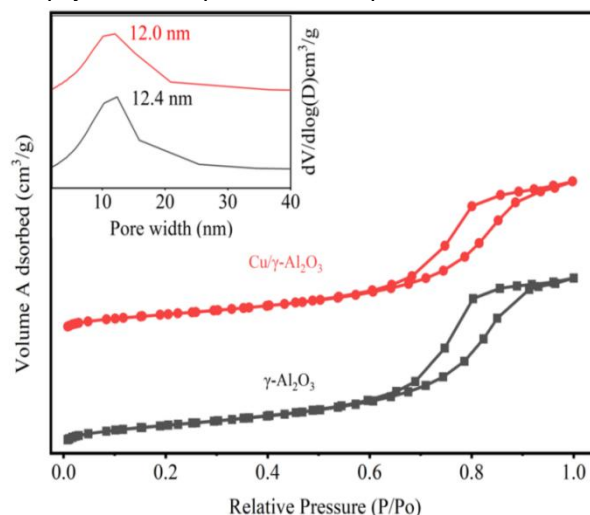


Figure 3.7 N_2 adsorption-desorption isotherm and pore size distribution of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$

Figure 3.shows the N_2 adsorption-desorption isotherm and pore size distribution of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$. It can be seen from the figure that the adsorption-desorption isothermal curves of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ are similar, and the N_2 isotherm has a significant hysteresis loop in the range of P/P_0 0.57~0.99, which is usually attributed to the existence of the catalyst intermediate pore structure. The pore size distributions of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ are concentrated at 12.4 nm and 12.0 nm, respectively. After the introduction of Cu, the specific surface area and mesoporous volume of $\gamma\text{-Al}_2\text{O}_3$ decreased slightly, and the dispersion of Cu on the support $\gamma\text{-Al}_2\text{O}_3$ was high, which had little effect on the pore size structure of the support.

Table 3.5 shows the structural properties of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ materials. The BET specific surface area and mesoporous pore volume of the following materials meet the technical requirements.

Table 3.5 Specific surface area and pore structure analysis of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$

Samples	$S_{\text{BET}}^a(\text{m}^2/\text{g})$	$S_{\text{ext}}^b(\text{m}^2/\text{g})$	$V_{\text{micro}}^c(\text{cm}^3/\text{g})$	$V_{\text{meso}}^d(\text{cm}^3/\text{g})$
$\gamma\text{-Al}_2\text{O}_3$	187	196	/	0.50
$\text{Cu}/\gamma\text{-Al}_2\text{O}_3$	164	172	/	0.45

^aBET specific surface area; ^b External surface area; ^c Microporous pore capacity;

^d Mesoporous pore capacity

3.3.6 H₂-TPR test

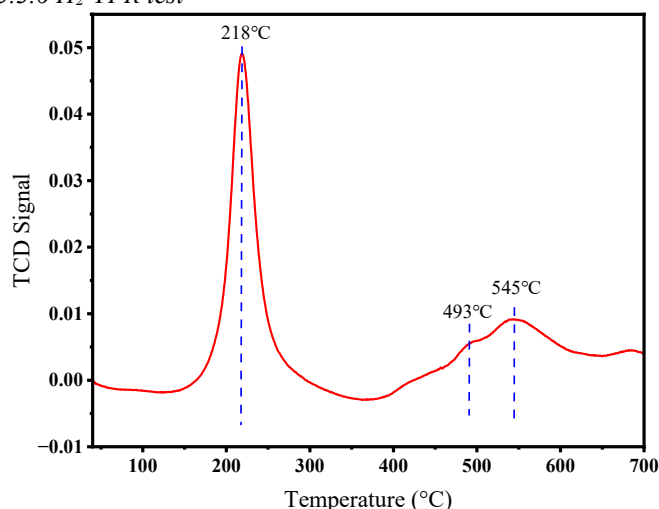


Figure 3.85 H₂-TPR test plot of Cu/γ-Al₂O₃ catalyst

Figure 3.85 shows the H₂-TPR curve of the Cu/γ-Al₂O₃ catalyst. The peak value of the reduction curve of the catalyst Cu/γ-Al₂O₃ showed three peaks, corresponding to temperatures of 218 °C, 493 °C, and 545 °C, and the relevant literature^[41] reviewed. The strong interaction of the carrier γ-Al₂O₃ with CuO results in a lower reduction temperature than pure CuO (the peak temperature of pure CuO is about 280 °C). 218 °C is the reduction peak of copper oxide on the surface of the catalyst to copper element. 493 °C is the reduction peak of Cu₂Al₂O₄ to copper element, and some of the Cu may enter the γ-Al₂O₃ framework and react with Al at high temperature calcination when the Cu/γ-Al₂O₃ catalyst is prepared by the immersion method. 545 °C is the reduction peak of Cu₂O to copper element.

3.4 Chapter Summary

In order to study the chemical and physical properties of Cu/γ-Al₂O₃ catalysts, a series of characterization tests were carried out on Cu/γ-Al₂O₃ catalysts, such as scanning electron microscopy (SEM), X-ray powder diffraction (XRD), pyridine infrared, N₂-physisorption desorption test, NH₃-TPD test, and H₂-TPD test, so as to obtain Cu. The structural properties and morphology of γ-Al₂O₃ catalyst. Scanning electron microscopy (SEM) showed that the metal Cu particles were dispersed on the surface of the support, which did not significantly damage the integrity of the original skeleton and retained the porous characteristics of the support. X-ray powder diffraction (XRD) showed that Cu was dispersed in the form of nanoparticles, Cu was highly dispersed in the carrier γ-Al₂O₃, the number of effective active sites of Cu was large, and the catalytic efficiency was high. NH₃-TPD and Py-IR characterization showed that Cu/γ-Al₂O₃ had two Lewis acid sites, one strong and one weak, which improved the acidity of Cu/γ-Al₂O₃. The results of N₂-physical adsorption desorption test showed that the pore size distribution of Cu/γ-Al₂O₃ was concentrated at 12.0 nm, and the specific surface area and mesoporous volume were slightly lower than those of γ-Al₂O₃. In addition, the results of H₂-TPR showed that in addition to CuO clusters, some Cu species entered the support

γ and Al₂O₃ underwent Cu-Al oxidation reaction with Al at high temperature.

IV. CONCLUSION

In this paper, the production of benzonitrile is mainly focused on the dehydroamination of benzyl alcohol catalyzed by supported catalysts. A series of supported metal catalysts were prepared by the equal-volume impregnation method, and the catalytic performance of these catalysts in catalyzing the ammonia oxidation reaction of benzyl alcohol was evaluated by fixed-bed reactor, and the catalyst Cu/γ-Al₂O₃ with better catalytic performance was screened. Catalyzed by this catalyst, benzyl alcohol catalyzes the main product of the ammoniation reaction is benzonitrile.

Through several experimental comparisons, we have preliminarily optimized the process conditions for the dehydroamination of benzyl alcohol catalyzed by Cu/γ-Al₂O₃ catalyst to prepare benzonitrile, and finally obtained a better process condition of atmospheric pressure, 350 °C, ammonia flow rate of 22 mL/min, 2 g catalyst, 20 % v/v reactant cyclohexane solution, and the conversion rate of benzyl alcohol under these conditions is 100 %, the selectivity of benzonitrile can reach 88.9%.

The reaction mechanism of catalyzing the ammonia oxidation of benzyl alcohol to benzonitrile, toluene, benzaldehyde, dibenzylamine and N-benzenebutylamine was studied, and the possible reaction pathways were proposed. In addition to direct dehydrogenation to form benzaldehyde, benzyl alcohol is partially dehydrated and condensed to form dimethyl ether; Dimethyl ether hydrogenation recomposes into benzyl alcohol and toluene, and some of them will be directly decomposed into benzaldehyde and toluene; Benzaldehyde dehydration and ammonia reaction to form unstable benzimine; Some animelimines will be directly dehydrogenated to form benzonitrile, benzimine can be converted to benzamine through dehydrogenation/hydrogenation, and some will remove ammonia and benzamine to form N-benzenthotriner. Benzamine can be dehydrated and reacted with benzaldehyde to form N-benzenemine, which is converted to dibenzylamine through hydrogenation/dehydrogenation. N-benzenebutylamine removes toluene to form benzonitrile.

In addition to the experimental results, we also characterized the support γ-Al₂O₃ and the catalyst Cu/γ-Al₂O₃ to analyze the reasons for the excellent catalytic performance of the Cu/γ-Al₂O₃ catalyst. In the copper catalyst prepared by ethanol wet impregnation method, in addition to the CuO clusters, some Cu species entered the carrier γ-Al₂O₃ and underwent Cu-Al oxidation reaction with Al at high temperature. The metal Cu particles are highly dispersed on the surface of the carrier in the form of nanoparticles, and the number of effective active sites of Cu is large, which has little impact on the pore size structure of the carrier, does not significantly damage the integrity of the original framework, retains the porous characteristics of the support, and has high catalytic efficiency. Cu/γ-Al₂O₃ has two Lewis acid sites, one strong and one weak, which improves the acidity of the catalyst.

V. REFERENCES

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