

# The Influence of Different Catalysts on the Environment and Urea Catalytic Efficiency

Danyang Zhang\*

Kharkiv Institute, Hangzhou Normal University, Hangzhou, 311121, China

\* Corresponding Author Email: 2021213103031@stu.hznu.edu.cn

**Abstract.** China is one of the world's top producers of agriculture, therefore expanding the urea market is crucial to supplying the country's expanding population. Agriculture has grown more dependent on nitrogen and urea as a result of population growth and other socioeconomic factors, which has led to excessive reliance on fossil fuels like coal and oil. Finding a suitable urea catalyst is vital since the urea industry's sustainability is being threatened from all angles by excessive energy consumption and high environmental emissions. Therefore, individuals prefer to hunt for ideal catalysts to increase efficiency among a number of parameters, including catalyst, reaction temperature, and reaction duration, in order to enhance the rate of urea and decrease the cost. In order to address the issues of the industry's overall level, ecology, and production structure, people start to screen and invent the catalysts from the metal and non-metal directions in terms of their activity, stability, and cost.

**Keywords:** urea synthesis, urea catalyst, environmental protection.

## 1. Introduction

The organic compound urea is made up of the elements C, N, O, and H. The majority of urea produced worldwide is utilized as nitrogen fertilizer because of its high nitrogen content (46%) and ease of conversion into  $\text{NH}_3$  in the soil. This helps to significantly increase grain output. The growth of the urea business is crucial to fulfilling the expanding demand because urea is currently one of the most significant nitrogen fertilizers [1]. Therefore, it is crucial to develop a process for producing "green urea" that uses less energy and is very effective. Researchers have also been working on the process of creating synthetic urea because urea has always had a significant impact on human life. In addition to the conventional method, urea can also be produced under certain circumstances using carbon monoxide and ammonia gas. The activity and selectivity of the electrocatalytic production of urea are still constrained by the inert nitrogen gas and the relatively weak chemical adsorption of carbon dioxide molecules on the catalyst surface; A substantial overpotential is needed to break the exceptionally strong C=O double bond and the  $\text{N}\equiv\text{N}$  triple bond; The simultaneous reduction of carbon dioxide and nitrogen inhibits the C-N coupling reaction during the synthesis of urea and results in a complicated product distribution [2,3]. But the production of conventional urea necessitates the use of around 80% of industrially produced synthetic ammonia, which is largely dependent on the interaction between high energy consumption and high carbon emission. High energy consumption, complicated machinery, and a multi-cycle synthesis procedure are needed to increase conversion efficiency. The new technique involves electrocatalytically combining  $\text{N}_2$  and  $\text{CO}_2$  to produce urea at standard temperatures and atmospheric pressure.

However, efficiency and energy consumption have not yet reached a level suitable for industrial manufacturing, regardless of the methods now in use. Consequently, finding a good catalytic approach and catalyst has turned into the key to boosting the efficiency in order to increase the rate and decrease the cost of the efficient synthesis of urea.

## 2. Catalysts

The most recent theoretical studies and practical experience indicate that Pd, Ni, and Cu can catalyze the synthesis of urea under microwave radiation or via electrochemistry. More Cu lines, Ti

systems, and other catalytic systems combined with nanotechnology for the catalytic production of urea have recently been discovered by numerous researchers. A novel kind of inexpensive catalyst with great efficiency and environmental protection is urea nanocatalyst.

In an aquatic setting, Chen Chen et al. demonstrated a technique for directly linking both  $N_2$  and  $CO_2$  to create urea. When the coupling event took place, the C-N bond was created by a thermodynamic spontaneous reaction between  $N=N$  and  $CO$  on  $TiO_2$  nanosheets utilizing electrocatalysts made of PdCu alloy nanoparticles [4].

Metallic and non-metallic catalysts make up the bulk of the categorization of urea production catalysts.

There are numerous classifications of catalysts used in urea production. In general, there are many different kinds of catalysts, which may be categorized into homogeneous and heterogeneous catalysts by reaction system, liquid and solid catalysts by state, soluble transition metal compounds, and peroxide catalysts, among others. Solid acid, organic alkali, metal, metal oxide, complex, rare earth, molecular sieve, biological, nano, and other types of catalysts are all examples of polyphase catalysts. According to the kind of reaction, oxidation, reduction, hydrogenation, dehydrogenation, and auxiliary catalyst according to their purpose [5].

### 2.1. Metal Catalysts

One of the key catalysts for the production of urea is metal. Metal catalysts with a wide range of applications include iron, cobalt, nickel, copper, chromium, etc. The iron catalyst, which has the characteristics of having high catalytic activity, good stability, and inexpensive price, is the one that is most frequently utilized. Iron catalysts have poor selectivity and are simple to induce side reactions, which have an impact on yield and quality.

### 2.2. Non-Metal Catalysts

A brand-new kind of catalyst that has just been invented is the non-metal catalyst [6]. Ionic liquids, organic catalysts, enzyme catalysts, etc. are examples of frequently used non-metallic catalysts. These catalysts benefit from strong catalytic activity, excellent selectivity, and accommodating reaction conditions. Non-metallic catalysts have a high cost and limited stability and lifetime, which are disadvantages. In a thorough comparison, metal and non-metal catalysts each have advantages and drawbacks. To fully exploit their individual advantages and enhance the yield and quality of synthetic urea, metal, and non-metal composite catalysts are frequently used in practical applications.

## 3. Influencing Factors

The catalyst, the reaction temperature, and the reaction duration are only a few of the variables that affect urea generation.

### 3.1. Catalysts

According to published research, adding OVs increases Pd1Cu1 /  $TiO_2$ -400's ability to activate  $N_2$  and  $CO_2$ , which boosts the catalyst's functionality and makes it easier to produce urea [7].

### 3.2. Light and Absorbance

It may be deduced that the diacetyl monooxime method was used to measure the urea concentration in the electrolyte. After heating, the reaction of the diacetyl monooxime with the acid produced a pink product, with the greatest absorbance at 525 nm. As a result, the relationship between the absorbance and urea content is linear [7].

According to the most recent theoretical studies and practical results, electrocatalytic coupling of  $N_2$  and  $CO_2$  can produce urea at room temperature and room pressure [2]. However, the process has a low selectivity. the existence of competition between non-coupled electrochemical reduction processes and selective C-N coupling. In order to increase the success rate of anchoring and the

successful synthesis of PdCu alloy nanoparticles, Chen Chen et al. synthesized the PdCu alloy nanoparticles on the original TiO and the OV-rich TiO<sub>2</sub> by co-reducing the metal precursor. This improved the overall selectivity [7].

#### 4. Debate

In order to prevent the greenhouse effect, the concept of "carbon neutrality" is crucial. Circulation and utilization of carbon dioxide are crucial, and one of the most important products for reducing carbon dioxide is urea. Because urea is one of the most important nitrogen fertilizers, the growth of the urea industry is crucial in order to meet the demand of the expanding population [1]. Around 80% of the world's ammonia supply is used to produce urea, mostly from the fixation of synthetic N<sub>2</sub>. Due to this molecular inertia, the fixation of the Earth's abundant nitrogen is a difficult scientific and technical problem. There is still a long way to go before catalyst stability and nitrogen fixation in urea. The process theory of urea production is still in its infancy, and a full theoretical calculation method has not been established, according to the overall trend of research on worldwide urea production. The hypothesis of the urea generation process is still being investigated. In the manufacture of urea, the immature production hypothesis has numerous flaws. The urea manufacturing system's control parameters are still primarily dependent on practical experience, with insufficient theoretically sound and precise control points. The manufacturing of urea involves a number of difficult-to-manage intermediate products and by-products, including ammonium, which is a highly corrosive intermediate product. The corrosion resistance of the by-product has a significant impact on the quality control of urea products [8]. The urea production system swings substantially, and it is necessary to reduce material consumption and increase system stability in order to reduce environmental contamination. The main focus and subject of research in urea production and the stability of the system are related to the safety, stability, economy, and environmental protection of the urea system.

#### 5. Challenges and Suggestions

China is now the world's largest producer and consumer of urea, with a national urea production capacity of about 80 million t/a, physical output of 71 million t, and operating rate of about 76% in 2015, according to statistics from the China Nitrogen Fertilizer Industry Association [9]. The urea industry in China is currently going through a crucial phase of innovation, development, transformation, and upgrading. There are both possibilities and obstacles in this phase. By 2018, it is predicted that the capacity for producing urea would be controlled at 76-78 million t/a, the capacity for backward production will be at least 10 million t/a, and the capacity utilization rate will rise to 85%–90%. In order to strike a balance between supply and demand, new, high-quality capacity will need to be created in order to remove and replace backward capacity if the aforementioned objectives are to be met. By 2020, the Ministry of Agriculture wants to stop using chemical fertilizers altogether. One thing that needs to change is how much chemical fertilizers are used. On the other hand, it should also be guaranteed that crops will be produced. The chemical fertilizer sector is actually being forced by this to go green. The urea industry can help the sector resolve overcapacity, adjust the industrial structure, improve and optimize the raw material structure, support the upgrading of product structure and quality, boost innovation capacity, raise the bar for energy conservation and environmental protection, and boost core competitiveness through transformation and upgrading [10]. The following are the key defenses and ideas for advancement.

##### 5.1. Improvement of the Overall Technology of the Industry

Large-scale urea equipment with an advanced technical level should be created for mass production, and the current inefficient production capacity should be gradually phased out. The outdated full-cycle procedure of aqueous solution should be eliminated in favor of cutting-edge steam

formulation technology. The new unit of 1 t urea product's maximum medium-pressure steam consumption shouldn't exceed 750 kg (2.4 MPa saturation). The choice of technology should also take into account China's indigenous technologies, such as the "efficient synthesis, low energy consumption urea technology" developed successfully by China Wuhuan Engineering Co., LTD., whose medium pressure steam consumption of 1t urea products is less than 750 kg (2.4 MPa saturation), ranking it at the top of the world. The conditional equipment should simultaneously strive for changes in energy-saving technologies. In order to lower the pressure steam consumption of 1 t of urea product to below 800 kg (2.4 MPa saturation), modern technology is employed to update the current equipment. The major goal of the transformation is to maximally raise the low-pressure steam's pressure in the high-pressure cycle so that it may be effectively utilized in the ensuing medium- and low-pressure decomposition and evaporation phases. To redirect the load from the high-pressure tower and lower the amount of medium-pressure steam used a straightforward medium-voltage system is put up. This system uses low-pressure steam heating.

New, high-performance corrosion-resistant materials should be created, and research and development spending should be boosted. China still has a long way to go in this area as overseas urea patent producers, huge steel firms, and research units already create their own proprietary materials. For as soon as feasible to produce their own urea-grade double-phase steel new materials, pertinent units must improve their cooperation. To increase service life, the equipment's corrosion resistance needs to be enhanced. As a result, there will be less anti-corrosion air in carbon dioxide gas. It will be safer for the exhaust gas system and easier to operate the exhaust gas cleaning system. Compressed power consumption, synthetic conversion rate, consumption, process exhaust gas, pollution emission, and all other related metrics will decrease.

## 5.2. Toward Eco-Friendliness

It is important to stress the issue of urea dust and ammonia pollution caused by granulation exhaust gas. To keep the emission of urea dust below  $50 \text{ mg/m}^3$ , the new device must set up a granulation washing and recovery system. Two techniques can be thought of for free ammonia in granulation exhaust gas.

(1) The pickling system is installed in the upper section of the urea dust washing. The free ammonia in the exhaust gas is recovered using sulfuric acid or nitric acid cycle washing to produce the byproduct ammonium sulfate or ammonium nitrate.

(2) Acid neutralization: To neutralize the free ammonia in the urea solution, a certain volume of sulfuric acid or nitric acid solution is fed directly into the urea melting pump intake. How to properly dispose of the byproducts, ammonium sulfate or ammonium nitrate, is the present issue with these two procedures. The investment is too great and the economic gain is too small if it is employed as a byproduct (crystallization or granulation). It is simple to accomplish, nevertheless, if the recovered by-product ammonium sulfate or ammonium nitrate solution is combined with the urea solution to generate ammonium sulfate-urea or ammonium nitrate-urea products. In particular, the second scheme directly combines the by-product with urea products, necessitating a re-examination of urea product quality requirements by the relevant authorities in order to support these various fertilizer and environmental protection measures. The treated granulation tail gas's ammonia mass content will be kept below  $50 \text{ mg/m}^3$ . A unique torch system might be taken into consideration for treating the process exhaust gas and accident emission of urea factories when environmental protection standards grow.

## 5.3. Optimization of Production Structure

To create industrial and specialty urea, automotive urea, and urea ammonium nitrate solution (UAN) the product structure needs to be adjusted [10].

Regarding the various production steps, it is discovered that synthetic ammonia is typically the biggest energy consumer throughout the entire urea synthesis process. Ammonia synthesis will exhibit a modest development pattern before 2030 due to the rise in demand for nitrogen fertilizers

[10]. Ammonia synthesis needs to be given a lot of consideration in light of China's efforts to conserve energy and reduce emissions in order to lower overall urea sector energy consumption and emissions. The primary energy source for coal ammonia (AC) synthetic coal is direct energy use, whereas the primary energy source for natural gas (ANG) synthesis of ammonia is direct energy use, production, and delivery of natural gas [10]. Therefore, the energy consumption throughout the urea production process can be significantly decreased by increasing the efficiency of natural gas or coal-related energy utilization. Due to its unique energy balance, coal continues to be the primary raw material used in China to produce synthetic ammonia. A limited amount of ANG synthesis for natural gas is employed in China due to its high energy intensity and expense, even though ammonia synthesis has been widely used in several nations. The widely used technique of manufacturing is still one that uses urea.

## 6. Conclusion

The catalytic synthesis of urea is reviewed in this study. The most prevalent catalysts and influences on the synthetic processes are introduced first. Metal catalysts have high catalytic activity, excellent stability, and low cost; however, the iron catalyst has poor selectivity and is prone to side reactions, which reduces yield and quality. In addition, non-metallic catalysts have favorable reaction conditions, high catalytic activity, and good selectivity. To improve the yield and quality of synthetic urea, both catalysts fully exploit their individual advantages. The debate around urea production and decarbonization is then covered. The issues and recommendations are then put forth. The domestic urea industry currently exhibits a stark overcapacity paradox, and the technology of different firms is uneven. As a result, the urea sector's technology is currently confronted with numerous problems and innovations. Products generate copious volumes of wastewater containing both human and animal urine during the urea synthesis process. If left untreated, this wastewater with a high urea level will break down into ammonia and other nitrogen-based pollutants, posing a major threat to the environment. Therefore, it is crucial to correctly treat the wastewater containing urea since, whether seen from an energy or environmental standpoint, other elements will also have an impact on the output.

## References

- [1] Krzywda, P., Rodrzywda, P., et al. Carbon-Nitrogen bond formation on Cu electrodes during CO<sub>2</sub> reduction in NO<sub>3</sub><sup>-</sup> solution. *Applied Catalysis B: Environmental*. 2022, 316, 121512.
- [2] M.H. Jang, M.F. Zhu, M.J. Wang, et al. Review on Electrocatalytic Coreduction of Carbon Dioxide and Nitrogenous Species for Urea Synthesis, *ACS Nano*, 2023, 17 (4), 3209–3224.
- [3] Alfian, M., Purwanto, W.W., Multi-objective optimization of green urea production, *Energy Science & Engineering*, 2019, 7(6), 292-304.
- [4] M. Wang, L.Y. Chu, Z.Y. Li, et al. Dinitrogen and Carbon Dioxide Activation to Form C–N Bonds at Room Temperature: A New Mechanism Revealed by Experimental and Theoretical Studies, *ACS Nano*, 2021, 12 (14), 3490–3496.
- [5] Sutradhar M, Pombeiro AJL, et al. Chapter 15 - Vanadium catalysts, *Vanadium*, 2021:415-443.
- [6] Baorong Hou, et al. *The Cost of Corrosion in China*. Springer, 2019.
- [7] C. Chen, X.R. Zhu, X.J. Wen, et al. Coupling N<sub>2</sub> and CO<sub>2</sub> in H<sub>2</sub>O to synthesize urea under ambient conditions, *Nature Chemistry*, 2022, 12: 717-724.
- [8] Y.Y. Li, D.M. Deng, H. Wang, et al. Controlled synthesis of Cu-Sn alloy nanosheet arrays on carbon fiber paper for self-supported nonenzymatic glucose sensing, *Analytica Chimica Acta*, 2022, 1190, 339249.
- [9] Y.H. Chen, Y.F. Lyu, X.D. Yang, et al. Performance comparison of urea production using one set of integrated indicators considering energy use, economic cost and emissions' impacts: A case from China, *Energy*, 2022, 254, 124489.
- [10] X.M. Chen, W.T. Tian, B.Y. Su, et al. Au nanoparticles on citrate-functionalized graphene nanosheets with a high peroxidase-like performance, *Dalton Transactions*, 2020, 43, 7449-7454.