

Clean Process for Catalytically Converting Waste Nitrogen-Containing Organics to a Syngas

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ABSTRACT

As an unconventional organic pollutant, nitrogen-containing organic waste gas is usually highly toxic, and its clean treatment is becoming urgent under the increasingly strict environmental protection requirements. The nitrogen-containing exhaust gas produced as tar precipitation after cooling down, and it is mostly eliminated by the combustion method to possibly recover heat, but it is easy to produce problems of NO_x emission and incomplete combustion. Catalysts for tar oil to convert it as a syngas generally include natural ore materials, transition metals, alkali metals, etc. Synthetic catalysts have controllable physical and chemical properties and are favored because of their high catalytic activity and low price. For the development of an efficient nitrogen-containing organic waste gas to retrieve resources as syngas, the catalyst is a highly important part. The development of catalysts and its process in this aspect is scarce and thus we combed here to provide meaningful guidance for the blossom of catalytic cracking approach.

Keywords: nitrogen-containing organic waste gas, catalytic cracking, synthetic catalysts

1. NITROGEN-CONTAINING ORGANIC WASTE GAS

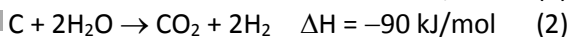
In recent years, emissions from human activities have far exceeded the upper limit of the natural environment bearing capacity. Serious environmental problems even threaten human survival and development. With the development of economy and

society, there are more and more sources of nitrogen-containing organic waste gas, such as acrylonitrile producing, coal combustion, high-temperature pyrolysis of biomass, exhaust gas denitration process, automobile exhaust emissions, etc. [1-3] Nitrogen-containing organic waste gases, such as organic nitriles, are highly toxic emissions and belong to the category of unconventional pollutants. In particular, nitrile compounds containing cyano groups are often toxic or carcinogenic, however there are few reports on the research of nitrogen-containing organic waste gas treatment technologies.

Carbon fiber production is one of the main sources of nitrogen-containing organic waste gas. At present, about 96% of carbon fiber production processes are based on the route where polyacrylonitrile as a precursor [4], which is a typical organic emission of cyanide exhaust gas. Acrylonitrile is pre-oxidized and carbonized to obtain the ideal carbon fiber yarn. The total nitrogen content in the exhaust gas will account for 26.4% of the raw material. With the development of society, the demand for high-performance carbon fiber materials is increasing, and it is expected that by 2020, it will increase from 58,000 tons in 2015 to 100,000 tons. [5] Therefore, the treatment of nitrogen-containing organic waste gas will be a key issue that needs to be urgently addressed. Although merit reviews may cover the elimination of biomasses or wastes, few reports focused on the conversion of valuable nitrogen-containing substances into syngas and therefore we summarized the most recent developments.

2. ELIMINATION METHODS FOR ORGANIC NITRILES

Waste-to-energy has been recognized a sustainable way to convert waste as resources by either eliminating organic nitriles or recovering energy. Organic chemicals containing energy has been previously studied (Eq. 1 to 3). [6] A process using superheated water vapor as an oxidizer and an energy carrier has been developed recently for the indirect gasification of organic carbons to produce syngas. In the process similar to traditional town-gas making in a gasification furnace at certain temperature the nitrile-fuel undergoes dehydration, separation of volatile components, cracking and gasification reaction, thus forming a tar-free crude synthetic gas. The synthetic gas produced has a high heating value and is free of secondary contaminations. Superheated water vapor is generated via an apparatus including thermal plasma technology or non-thermal plasma discharge for implementing the process. [7]



2.1 Combustion conversion

Combustion is a violent oxidation reaction process, and a traditional method for treating organic waste gas. The combustion method can be divided into a direct combustion method and a catalytic combustion method. The direct combustion method has some limitations due to its high temperature, explosion, and secondary pollution. The catalytic combustion can reduce the temperature of the reaction, improve the reaction efficiency, and the waste heat can be further recycled. However, for the catalytic combustion of nitrile compounds, how to avoid secondary pollution caused by deep oxidation is an important issue that needs to be solved, and the adaptation to changes in the concentration of the raw material gas will also be limited.

2.2 Catalytic oxidation

Catalytic oxidation means that at a certain temperature, nitrile compounds and oxidants undergo catalytic oxidation reactions on the catalyst surface, so that they can be removed by degradation. Commonly used catalysts are transition metal (including noble metal) catalysts supported on different supports. Nanba's group [8] did a lot of work on the selective catalytic oxidation of propionitrile, screened a large number of different catalysts, and found that at 350 °C, the conversion rate of Cu/ZSM-5 for propionitrile can reach 100%. The selectivity of N₂ can reach 80%. The

selectivity of non-toxic target products in catalytic oxidation process is an important research content, and the adaptation of the composition change and complexity of the feedstock gas remains to be studied.

2.3 Catalytic cracking

Catalytic cracking technology is mostly used in the production of olefins in industry, and the process of cracking tars to produce small molecules of combustible gas. [9, 10] Under the condition of high temperature catalytic cracking, it will also have a good treatment effect on nitrogen-containing exhaust gas. Organic exhaust gas can be cracked into small molecular gases such as H₂, CO, and CH₄ to realize the resource utilization process. Meanwhile, by using a suitable catalyst and suitable reaction conditions, the nitrogen in the nitrile exhaust gas can also be converted into non-toxic N₂ with high selectivity. However, the reaction temperature required for this process is relatively high, and the catalyst is prone to carbon deactivation.

For the exhaust gas generated during the carbonization stage of polyacrylonitrile carbon fiber, the gas temperature is above 600 °C, the composition is complex, and it also contains HCN, NH₃, nitrile organic compounds, etc. The catalytic cracking method fully meets the high temperature characteristics of the exhaust gas, neither require special cooling treatment, nor cause the problem of tar condensation and clogging. The waste heat of the exhaust gas is used, and the cracked products H₂, CO, and CH₄ are obtained at the same time, so that the exhaust gas can be treated as a resource. Catalytic cracking is a treatment method worth more research attention.

3. APPLICATION OF CRACKING CATALYSTS FOR NITROGEN-CONTAINING ORGANIC WASTE GAS AND TAR GAS

Catalysts remain a key role in the removal of nitrogen-containing organic waste gas by catalytic cracking. So far, there have been relatively few studies on the conversion treatment of nitrogen-containing organic waste gas, especially that containing high-boiling tar mixtures. In addition to comprehensively investigating the catalysts for the conversion of nitrogen-containing organic waste gas, it is also necessary to include catalysts for tar cracking, especially biomass tar cracking. Generally, the catalysts for catalytic cracking can be roughly divided into two categories: natural ore catalysts and synthetic catalysts.

3.1 Natural ore catalysts

Natural ore-based catalysts are produced in nature with relatively complex components, but usually contain several major metal elements. The common point of this type of catalysts is that they can be used directly or after simple physical treatment such as heating and calcination. It has abundant sources and is convenient to handle after use. Their cost is much lower, compared with artificially synthesized catalysts. Therefore, the catalytic performance of some natural ores has attracted researchers' enthusiasm. Dolomite, olivine, clay ore, iron ore, etc. have been surveyed more on natural ore catalysts.

Devi et al. [11] led a real biomass gasification tar gas from the gasification fluidized bed and passed through a fixed bed reactor equipped with dolomite packing. As the bed temperature increased from 800 °C to 900 °C, the tar content in the outlet gas continued to decrease. At 900 °C, the water-soluble heterocyclic compounds can be completely converted, and overall export tar as polycyclic aromatic hydrocarbons were removed by 90%. Dolomite as the catalyst increased the content of fuel gas at the outlet, especially in the presence of water vapor, the H₂ content was greatly improved. In addition, Berrueco et al. [12] studied the effect of dolomite on the removal of biomass tar in a pressurized fluidized bed, and proposed that changes in tar yield and composition are subject to two competing reactions, i.e. polymerization of tar, and dealkylation, dehydrogenation and cracking reactions of tar. In a dolomite bed, the cracking will be the main reaction, tar reduced and combustible gas increased.

Foscolo [13] and Devi [11] compared the catalytic effects of olivine and dolomite on tar decomposition in a fixed bed and a fluidized bed, respectively. Olivine had slightly lower permanent gas yield and tar removal activity than dolomite, suitable for fluidized bed reactors because of its better mechanical strength. Corella et al. [14] found in a gasification fluidized bed contain less tar, NH₃ and particulate matter. In addition, in calcined dolomite, the tar content in the product gas was only 60% of the case of olivine, but the amount of particles or dust produced was 4-6 times that of olivine, and the NH₃ content in the product also became high.

Adjaye et al. [15] and Simell et al. [16] tested amorphous silicon-aluminum oxide and silicoaluminous clay mineral (13 wt% Al₂O₃, 86.5 wt%, 100 m² g⁻¹) catalyst in a fixed bed reactor, the catalytic effect was in the following order: commercial nickel-based catalysts (Ni/Al₂O₃) > dolomite > activated alumina > silica-alumina clay > inert silicon carbide. This type of catalyst

enhanced the reaction activity of tar cracking, but had almost no activity on gas phase reactions such as water vapor shift reaction, steam reforming reaction, dry reforming reaction and so on.

Cypers et al. [17] studied the effect of iron ore on coal cracking showed the hematite had a greater impact on coal cracking, and Tamhankar et al. [18] given similar results: iron ore/silica catalyst had a good activity for benzene cracking and a high selectivity for methane. But, Simell et al. [19] found that both ore materials (sintered and pelletized iron ore) had lower tar elimination activity than dolomite.

3.2 Synthetic catalysts

Synthetic catalysts are obtained by artificial chemical synthesis. The performance of this type of catalyst can be adjusted artificially, and it has better specificity and reactivity for the specific reaction process. [20, 21] But the cost is usually more expensive than ore-based catalysts. This type of catalyst can be roughly divided into transition metal-based catalysts, carbon-based catalysts, alkali metal-based catalysts.

Among precious metal catalysts, Rh-based catalysts are more active than other catalysts in their catalytic reforming reactions. Ammendola et al. [22] studied the effect of sulfides in tar on the performance of Rh-based catalysts. At 200 ppm H₂S reaction conditions, the Rh active sites distributed in 1% Rh/Al₂O₃ were poisoned, resulting in a decrease in the catalytic reforming performance. However, in the 1% Rh-LaCoO₃/Al₂O₃ catalyst, the LaCoO₃ layer of the perovskite structure effectively protected Rh from poisoning reactions by sulfides. Iida's group [23, 24] prepared Ru as a catalyst on 12SrO-7Al₂O₃ support for the steam reforming of toluene and dodecyl. Ru precursor, catalyst calcination and pretreatment conditions will greatly affect the catalytic activity and stability of the catalyst. The active oxygen species in the support 12SrO-7Al₂O₃ promoted the CH_x oxidation reaction on the surface of Ru metal, reduced the carbon deposition on the catalyst, and improved the stability. In addition to pure noble metal catalyst support, there are also studies using noble metals Pt, Pd, Rh and Ru as additives to traditional Ni/CeO₂/Al₂O₃ catalysts for biomass vaporization. [25] The results showed that the modification effect of Pt was the best, and it only needed to add 0.01 wt% to produce obvious modification effect. The characterization results showed that a Pt-Ni alloy component was formed in the Pt/Ni/CeO₂/Al₂O₃ catalyst.

Although precious metal catalysts with relatively low precious metal content can have high catalytic

performance, the production cost of precious metal catalysts is still unsatisfactory, and there are certain limitations for the large-scale adoption in actual production. Therefore, transition metals such as Co, Fe, Mo, etc. have been applied to tar steam reforming. [26-29] Furusawa et al. used naphthalene as a model compound for tar, and compared the steam reforming performance of Co/MgO and Ni/MgO [30] showed that Ni/MgO catalyst, excess H₂O was activated, resulting in the reduced activity of the nickel-based catalyst, and Co/MgO had a higher catalytic activity. Efstathiou et al. [31] tested Fe/50Mg-50Ce-O catalyst for CO₂ adsorption enhanced phenol steam reforming reaction. When loading 5 wt% Fe, the catalyst's performance was the best, with relatively high yield of H₂, and the smallest amount of carbon deposit, which was also superior to commercial nickel-based catalysts. When the loading of Fe was 10 wt%, the carbon deposition of the catalyst was the most serious. The Mossbauer spectrum found that the 5 wt% Fe/50Mg-50Ce-O after use had a higher Fe²⁺/Fe³⁺ ratio. Tomishige's group [32] studied the steam reforming reaction of tar in fir cracking process with Ni-Fe/Al₂O₃ bimetal catalyst showed that it was better than that of the single metal catalyst. An alloy phase of Ni-Fe was formed in the bimetal catalyst, and Fe atoms in the alloy were enriched on the catalyst surface. During the reaction, Fe atoms promoted the production of active oxygen, strengthened the reaction of tar conversion, and suppressed the generation of carbon on the catalyst surface.

4. DEVELOPMENT OF NOVEL CATALYSTS FOR NITROGEN-CONTAINING ORGANIC WASTE GAS

4.1 Carbon-based catalyst

Coke and activated carbon are inexpensive and porous, can be used as catalysts or catalyst supports for hydrocarbon conversion and tar cracking. [33, 34] The use of a carbon-based catalyst for tar elimination is related to its own pore size, specific surface area, ash and mineral composition. These physical and chemical properties are determined by the carbon-based catalyst precursor and the carbonization process. However, carbon-based catalysts are easily deactivated due to carbon deposits blocking pores and a reduction in specific surface area, and they are lost by participating in oxidation reactions during the reaction. Based on these characteristics, many researchers have used carbon-based catalysts for tar conversion reactions. Wang et al. [35] directly used coal coke for the in situ reforming reaction of tar produced in lignite cracking

and gasification. After the coal coke was subjected to an additional 10 min of steam treatment, the amorphous carbon structure, electron-rich elements (such as O) became more, and the specific surface area became larger. Under gasification conditions, the tar yield dropped to 1.82%. After metal loading, the coke catalytic activity can be further improved. Zhang et al. [36] found that the conversion activity of coke after Fe loading was better. The catalytic effect of biomass coke-supported iron was better than that of coal coke-supported iron. It seemed that specific surface area and pore volume were not the main determinants. The active components in coke and the amorphous carbon structure of coke had a great influence on the activity. Min et al. [37] reached similar conclusions that the activity of the coke-supported iron or nickel catalyst was higher than that of the coke itself for the tar steam reforming reaction. Bhandari et al. [38] prepared biochar, activated carbon and surface acidified activated carbon from biomass, and compared their activities in toluene steam reforming, all three showed conversion activity with conversion rates of 69-92%.

4.2 Alkali metal

The alkali metal is a monovalent metal element of the first main group in the periodic table, they have strong electropositivity and reactivity, and can catalyze the gasification of carbonaceous substances in the form of carbonates or supported on other materials. [39] Lee et al. [40] studied the gasification of straw on a Ni/diatomite catalyst and found that adding Na₂CO₃ to the reaction system can significantly increase the gas yield. Na₂CO₃ promoted the liquefaction process of straw (cracked into oil), and the Ni-based catalyst could promote the reaction of cracking oil to gas. The relationship between the amount of gas produced and the alkali metal carbonate was as follows: Li < Cs < K ≤ Na. Kuchonthara et al. [41] investigated the effect of K₂CO₃ addition on lignin gasification. K₂CO₃ could accelerate the rate of lignin vapor gasification reaction, but had no effect on the lignin conversion rate. Meanwhile, K₂CO₃ also had decomposition activity for the tar produced by lignin gasification, making the final gas product more. After adding K₂CO₃ to the porous material γ-Al₂O₃ and lignin mixed system, the gasification rate and conversion rate were significantly improved. When the reaction temperature reached 800 °C, the lignin was completely gasified. There is a large amount of K and a small amount of Na in the biomass in nature. The soluble alkali metal salt usually exists in the ash produced by the gasifier, which can be directly used

as a catalyst for tar conversion, and the problem of ash waste disposal is solved together. Hognon et al. [42] compared the steam gasification process of different biomass on a hot balance, and discussed the effect of the inorganic elements content in the biomass on the reaction process. They found that the presence of K in the biomass promoted the reaction. When the content of K in the biomass was high, the gasification reaction rate remained constant during most of the reaction process, and increased slightly at high conversion rates. For biomass with lower K content, the reaction rate decreased with the increase of conversion rate. Similarly, during the study of low-level coal gasification, co-gasification with biomass or the introduction of biomass ash will have a great impact on the gasification reaction, and alkali metals and alkaline earth metals in ash will promote the reaction. [43-45]

4.3 Combination of catalysis and plasma cracking

In our group, we have prepared Ni/CeO₂/CaO-MgO a hybrid catalyst exhibited excellent activity in the catalytic conversion of cyano-containing exhaust gases. The total gas yield of small molecular gases increased by 231.5% and the amount of HCN decreased by 91.5% at 650 °C under steam introduced compared to that of blank experiment. [46] During the steam reforming of model compound of benzonitrile, Ni/CeO₂/CaO-MgO kept stable performance during 16 h test with the benzonitrile conversion of 100% and low yield of HCN. It was believed that exists of the CaO in the catalyst improved the nickel reducibility making more metallic nickel active sites available. The synergy effects of CaO and CeO₂ could promote the oxygen species reacting with the coke precursor or carbon deposits, which inhibited the coke formation.

Although the carbon deposition over the used Ni/CeO₂/CaO-MgO catalyst was 1.4% that was much less than that of other catalysts, frequent refreshment of the reactor was needed. Regarding this aspect, we assembled dielectric barrier discharge (DBD) onto the catalyst further improve the durability to form hybrid reaction. It was found that plasma combined with catalysis have high performance of the conversion and durability. A pilot scale of treatment process for cyano-exhaust gas converting to syngas demonstrated its applicability in a carbon fiber manufacturer in Jiangsu Province, eastern of China.

5. PERSPECTIVES

The clean treatment technology of nitrogen-containing organic waste gas is receiving more and

more attention. The catalytic cracking pathway can crack organic waste gas into small molecular gases such as H₂, CO, and CH₄, and increasing the proportion of combustible components in the product will help achieve the goal of resourceful treatment. The development of efficient catalytic cracking catalysts is a core topic, and it is necessary to comprehensively consider the performance of catalyst conversion, selectivity, and durability according to the treatment goals. How to obtain synthetic catalysts with lower cost and controllable performance is an important research topic. The development of novel catalysts and their combinations with plasma technology provides richer options for the research community. The pursuit of higher catalytic performance and lower cost requires more effective synthesis strategies, as well as a better understanding of the relationship between catalyst structure, components and performance.

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