

Research Progress in Catalytic Desorption of Organic Amine CO₂ Absorbent Solution

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Abstract: In this paper, the research status of CO₂ catalytic desorption regeneration technology in amine absorption system was reviewed. The types, characteristics, advantages and disadvantages of heterogeneous catalysts and the challenges faced were introduced in detail. The main factors affecting the desorption and regeneration performance of catalysts were summarized. Finally, the current situation of catalytic desorption regeneration for CO₂ capture after combustion was analyzed, and the future research trend was prospected.

Keywords: Chemical Absorption Method; Catalytic Regeneration Technology; Heterogeneous Catalyst.

1. Introduction

Since the Industrial Revolution, global greenhouse gas emissions have been increasing, and the greenhouse effect has become increasingly serious. Climate change has become a serious challenge for us. Massive CO₂ emissions aggravate the greenhouse effect, leading to a series of international environmental problems such as rising sea level, melting glaciers and ocean acidification, and arousing the attention of human society on the change of ecological environment [1].

The chemical absorption method stands out as the most successful technology due to its advantages, including a straightforward process flow, rapid reaction rate, substantial absorption capacity, and well-established techniques. It is one of the most extensively utilized post-combustion CO₂ capture technologies. Nevertheless, this method also faces challenges, such as limited desorption capability and elevated energy consumption [2].

In this paper, we introduce and discuss the types and characteristics of various heterogeneous catalysts utilized for absorbent regeneration, as well as analyze the catalytic performance of these catalysts. We review the mechanisms of CO₂ desorption and summarize the impact of different parameters on the efficiency and energy reduction in catalytic CO₂ desorption. Lastly, we summarize the low-energy CO₂ absorption-desorption processes and outline potential future research directions to guide ongoing studies.

2. Heterogeneous Catalyst Types

2.1. Metal Oxide Solid Acid Catalyst

Metal oxides are a class of solid acid catalysts which have been widely used in commercial applications. Metal oxide nanoparticles catalyze CO₂ regeneration in both physical and chemical aspects. The physical enhancement of desorption is mainly due to the Brownian motion of metal oxide nanoparticles in amine solution, which is easy to break the bubble, increase the mass transfer surface area, and reduce the mass transfer resistance at the gas-liquid interface, thus greatly increasing the CO₂ desorption rate [3]. In 2011, the Idem team of the University of Regina [18] first introduced γ -Al₂O₃ as the desorption catalyst of 5mol/L ethanolamine (MEA) absorber system, and the regeneration temperature was reduced to 90~95°C, and the regeneration energy

consumption was reduced by 27%. Since then, metal oxides have been widely studied as desorption catalysts for amine systems. The researchers found that V₂O₅ [22], MoO₃, Ag₂O [23], Nb₂O₅ showed better catalytic desorption and regeneration performance due to the presence of both B acid and L acid sites, significantly higher than metal oxide catalysts with only L acid sites. However, MoO₃, V₂O₅ and Ag₂O are easily dissolved in the desorption process of organic amine absorbers, so their application may be limited. For this reason, FAN et al. [24] prepared TiO(OH)₂ using isopropyl titanate as a precursor system, and the abundant hydroxyl group on its surface can protonate protons ethanolamine was transferred to HCO₃⁻, and the desorption catalytic performance was stronger than TiO₂. Metal oxides as desorption catalysts have certain commercial prospects, but some oxides have low specific surface area, and more efficient catalytic materials can be obtained by transition metal modification in the future.

2.2. Molecular Sieve Solid Acid Catalyst

Zeolites are porous crystals with regular pore structure and high specific surface area, consisting mainly of zeolites (such as HZSM-5) and mesoporous silicon materials (such as SBA-15, MCM-41, and KIT-6). Molecular sieves are silicate and aluminosilicate crystals, with a three-dimensional crystal structure, mainly composed of silicon, aluminum and oxygen atoms [4]. The Al-O-Si bond in the molecular sieve structure provides pores, cavities and channels with regular size and arrangement, which is a unique catalytic material containing a precise single microporous structure [5]. Because of its large specific surface area, it is widely used in gas adsorption, petroleum processing, petrochemical industry, fine chemical industry and daily chemical industry. The solid acid catalysts such as MCM-41 and HZSM-5 used in the CO₂ desorption regeneration process were synthesized by hydrothermal method, and the preparation period was long. However, the application of molecular sieve still reduces the catalyst cost [6].

HZSM-5 exhibits high selectivity, a favorable silicon-to-aluminum ratio, and adjustable acidity; thus, it is the most prevalent molecular sieve catalyst employed for CO₂ desorption. Its CO₂ desorption catalytic performance has been reported to surpass that of γ -Al₂O₃. HZSM-5 exhibited higher catalytic activity than γ -Al₂O₃ owing to its superior mass transfer coefficient and more numerous BASs [7]. MCM-41 is

a typical mesoporous molecular sieve with highly ordered porous structure, large specific surface area and high thermal stability[8].

The surface of MCM-41 is rich in silicon hydroxyl and can be modified. The results show that the catalytic desorption performance of MCM-41 can be improved by modifying MCM-41 with different metals to generate new acid sites on the surface[9]. SBA-15 molecular sieve has the advantages of large pores, large mesoporous surface area and good thermal stability [10]. With SBA-15 carrier, the catalytic desorption performance of the catalyst was improved by increasing the number of active sites and improving the mass transfer performance. KIT-6 mesoporous molecular sieve has a three-dimensional porous structure, has a large pore size and high thermal stability [11]. These characteristics are conducive to the high dispersion of active components on the surface of KIT-6 and the rapid transfer of reactants and product molecules in the pore channels, thus improving the catalytic performance of KIT-6 supported catalyst.

2.3. Organic Skeleton Materials and Derivatives Thereof

Metal-organic skeleton material is a crystalline porous material with periodic network structure formed by self-assembly of metal ions and organic ligands, which has the advantages of high porosity, low density, large specific surface area, regular pore, adjustable pore size, diversity of topological structure and clipability. The coordination unsaturated sites on the metal clusters and their charged/coordination compensating groups confer B-acidity and L-acidity on the MOFs material. MOFs have excellent catalytic performance [12]. Using MOFs material as precursor, Wang Lidong's research group synthesized a series of MOFs derivative catalysts with excellent catalytic desorption activity. Using Ce-BTC as the precursor, CeO₂ rod-like structure with porous structure was formed through high temperature treatment, and HPW with different mass ratios of heteropolylic acid was further modified on its surface, showing excellent CO₂-catalyzed desorption and regeneration activity in 5mol/L MEA amine solution system. The CO₂ desorption capacity and desorption rate were increased by 38.1% and 166% respectively, and the energy consumption was reduced by 29.4%[13].

2.4. Nano Carbon Materials

Nano carbon materials are carbon materials with at least one dimension of dispersed phase scale less than 100 nm. The abundant weak acid sites on the surface of nano carbon materials can effectively increase the rate of CO₂ desorption and regeneration when used in amine absorbent system. Li Xiaojing et al. [14] from Dalian University of Technology investigated the desorption and regeneration process of a series of non-acidic carbon materials for amine absorbents, and found that carbon materials can significantly increase the CO₂ desorption amount by 47.1%~72.3%, and reduce energy consumption by 32%~42%. Compared with solid acid catalysts, carbon materials have similar desorption performance, but better stability.

3. Factors Influencing Catalytic Performance

Both the physical and chemical properties of solid acid catalysts can influence the CO₂ desorption performance

during aqueous solvent regeneration. This study investigates the catalyst to identify the key factors affecting its catalytic desorption performance, thereby providing theoretical support for the future synthesis of nanocatalysts with enhanced overall performance.

3.1. Effect of Physical Structure of Catalyst on Catalytic Performance

According to the literature, the mesoporous area, total specific surface area and average pore diameter of catalyst are the three key physical structural characteristics that affect the desorption performance of catalyst. The results of Idem et al. [15] show that HY>HZSM-5> γ -Al₂O₃ in order of total specific surface area, which is attributed to the fact that HY molecular sieve is a powdered solid, which has a large comprehensive consideration of specific surface area and mass transfer. In general, the larger the mesoporous area of the catalyst, the better the catalytic performance. According to the mesoporous surface area, the order is γ -Al₂O₃>H-ZSM-5>HY. The experimental data also confirm that HY has the worst catalytic desorption effect. One of the research directions of CO₂ desorption catalysts in the future is to search for new nanomaterials and synthesize heterogeneous catalysts with large and medium pore area and suitable average pore size.

3.2. Effect of Chemical Structure of Catalyst on Catalytic Performance

According to literature reports, acid strength, B-acid site, basic site and other chemical properties are the main structural factors affecting catalyst performance. The acidic sites of heterogeneous catalysts include L-acid sites and B-acid sites, and significantly affect the activity of solid acid catalysts in low temperature amine solvent regeneration. It has been found that there is a direct relationship between the total acid site of the catalyst and the rate of CO₂ desorption and energy consumption, so the acid strength of the catalyst is another chemical structural factor that must be considered. Acid strength is the ratio of the strong acid site divided by the total surface acidity [16].

The physical and chemical properties of catalysts do not affect the performance of CO₂ desorption in isolation. Researchers at home and abroad have studied the effects of catalytic desorption reactions nature, often need to consider both physical and chemical structural properties.

3.3. Effect of Catalyst Addition Amount on Catalytic Performance

The amount of catalyst added affects the catalytic desorption performance of the catalyst. Li Xiaojing et al. [17] investigated the influence of three kinds of multi-walled carbon nanotubes (MWCNT, MWCNT-COOH, MWCNT-OH) on the desorption of CO₂ in AEE aqueous solution under different addition amounts: the desorption effect increased with the increase of catalyst within a certain range. Liang Zhiwu's research group [18] found that in the process of catalytic desorption, γ -Al₂O₃ mainly acts in the region with low CO₂ load. The experimental comparison and analysis of the catalytic performance of different additive amounts of γ -Al₂O₃, compared with the blank experiment without adding catalyst, The CO₂ desorption capacity increased from 1.54mol to 1.67, 1.91 and 2.06 mol respectively, and the energy consumption decreased from 5.9MJ/kg CO₂ to 1.67, 1.91 and 2.06MJ/kg CO₂ respectively. The desorption data show that

the increasing use of solid acid catalyst can improve its catalytic performance.

4. Conclusion and Prospect

Chemical absorption is a mature CO₂ capture technology, but high energy consumption and high cost limit the commercial application of carbon capture technology. Adding solid acid-base catalyst to amine absorber can change the reaction path, improve the CO₂ desorption rate during low temperature regeneration, reduce sensible heat and latent heat, significantly reduce the input energy and reduce the overall energy consumption of regeneration, which is a new technology with potential application value. In this paper, the desorption and regeneration technology of amine absorption system is summarized and analyzed comprehensively from the types of catalysts and the factors affecting the performance of catalysts.

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