

FACTORS AFFECTING CATALYST ACTIVITY IN THE STEAMREFORMING PROCESS

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Abstract:

Developing new, highly efficient catalytic systems that are resistant to H₂S and coking—and based on cost-effective feedstock—as well as exploring innovative methods for processing heavy oil residues, constitutes a significant scientific and technical challenge. The objective is to establish the scientific foundations for processing (reforming) hydrocarbon feedstocks using sulfur-tolerant nickel catalysts and for converting oil refining residues into hydrogen-rich gas through microwave irradiation.

Keywords: sulfur resistance, coking, coke resistance, carbon sorbents, adsorbents, nanoscale catalysts, iron-nickel catalysts, phase transformations, C–H bond cleavage/cracking, spectroscopic methods, rapid destruction, decomposition, catalyst deactivation.

Introduction

The harsh conditions of the steam reforming process impose a number of requirements on both the catalysts themselves and their supports. Steam reforming catalysts are evaluated based on a combination of properties: activity, selectivity, thermal and chemical stability, mechanical strength, and hydraulic resistance.[1] These requirements are not exhaustive. The primary negative factor affecting catalyst activity is carbon formation, which typically leads to reduced activity and catalyst degradation.[2] A malfunction in the feedstock desulfurization system can lead to catalyst deactivation through the poisoning of active catalytic sites (resulting in the formation of inactive metal sulfides). Consequently, resistance to sulfur-containing compounds is a key requirement for catalysts used in the steam reforming of hydrocarbon feedstocks.[3] To meet this need, noble metals (Rh, Ru, Ir, Pt)—supported on materials such as α -Al₂O₃, CeO₂, TiO₂, and ZrO₂—are employed as active components, as they are resistant to both coke formation and sulfur poisoning. However, the cost of platinum-group metal catalysts is 100–150 times higher than that of nickel-based catalysts, while their activity is virtually comparable.[4][5]

Most tubular steam reforming reactors operate at temperatures exceeding the Tammann temperature for nickel ($T_T = 1/2T_{\text{boy}} = 581^\circ\text{C}$), which inevitably leads to the sintering of nickel particles. Sintering causes an increase in nickel particle size, resulting in reduced dispersion of the nickel particles on the support surface and a consequent decrease in the catalytic activity of the system as a whole. Sintering is a highly complex process that depends on numerous parameters, such as the reaction environment, the catalyst structure and composition, and the support morphology. High process temperatures and high partial pressures are factors that accelerate sintering.[6][7]

Methodology. The study is based on analysis of published investigations and reaction schemes. The manuscript describes in situ transmission electron microscopy (TEM) observations of Ni/MgAl₂O₄ sintering at 500°C, 30 atm and an H₂O:H₂ ratio of 10:1, together with DFT calculations, analysis of sulfur-hydrogenation and gas-purification reactions, and consideration of carbon-formation mechanisms.

The sintering mechanism was investigated in [1] using in situ transmission electron microscopy. The sintering of Ni particles supported on MgAl₂O₄ was studied at $T = 500^\circ\text{C}$, $P = 30$ atm, and an H₂O:H₂ ratio of 10:1. It was demonstrated that the sintering mechanism can be described as the migration and agglomeration of active particles on the surface of the spinel-structured support [2].

Particle movement is driven by the diffusion of Ni₂-OH dimers on the nickel surface. This hypothesis correlates satisfactorily with DFT calculations [1]. It should be noted that at lower temperatures, the duration of the process does not affect metal particle size. This theory applies to processes conducted at temperatures up to 580°C. An increase in the sintering rate of metal particles on the support surface in an H₂O:H₂ atmosphere is observed when the temperature rises to 600°C or

higher [3]. It is also noted that the influence of hydrogen partial pressure on particle sintering increases with rising temperature (Figure 1).

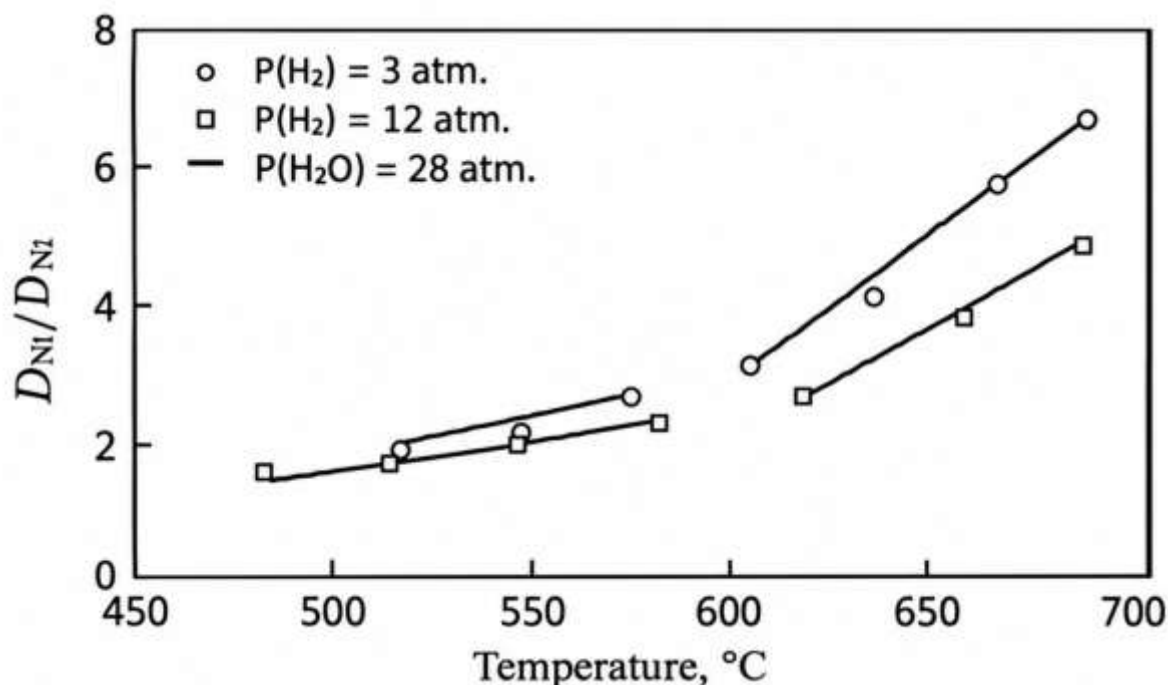
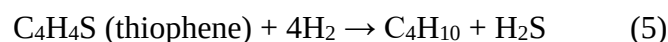
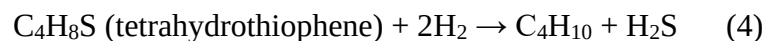
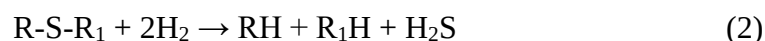


Figure 1. Dependence of the relative size of nickel particles on temperature after calcination for 700 h.

At elevated temperatures, particle sintering proceeds via a redeposition mechanism (Ostwald ripening). This mechanism can be described as the migration of atoms across the support surface. At elevated temperatures, particle sintering proceeds via a redeposition mechanism (Ostwald ripening). This mechanism can be described as the migration of atoms across the support surface.

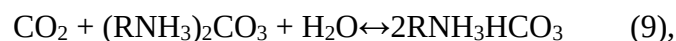
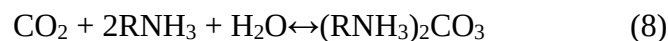
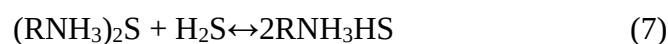
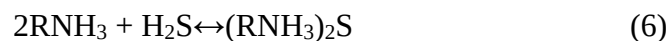
Results

The analyzed studies show that catalyst activity is strongly affected by nickel sintering, sulfur poisoning, and carbon deposition under steam-reforming conditions. The hydrogenation of sulfur-containing organic compounds is described by the following reactions.



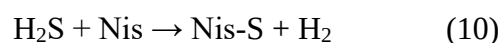
All the reactions listed above have high equilibrium constants within the operating temperature range of desulfurization reactors. The conversion of the initial organic compounds is virtually complete. As can be seen from reactions 1–5, following hydrogenation, the sulfur in the feedstock remains in the form of gaseous H_2S .

Next, to reduce the hydrogen sulfide content in the gaseous feedstock, alkanolamine purification is carried out. Aqueous solutions of monoethanolamine (MEA) are the most common absorbents used in industry. CO₂ is also absorbed during this process. The reactions of H₂S and CO₂ with MEA are described by the following overall reactions [4]:



where R is the OHCH₂CH₂ group.

At low temperatures, the reactions proceed from left to right, whereas at high temperatures, they proceed from right to left. In the first case, H₂S and CO₂ are bound by the adsorbent; in the second, the adsorbent is regenerated, and the absorbed acidic gases (H₂S and CO₂) are released. After alkanolamine purification, up to 30 ppm of hydrogen sulfide remains in the gas. However, this concentration is critical for PRM catalysts; this amount of hydrogen sulfide is sufficient to deactivate the active sites of the catalytic systems through the chemisorption of H₂S on the surface of Ni sites (Reaction 10).



This chemical interaction occurs only when the H₂S:H₂ ratio in the gas phase does not lead to the formation of massive sulfide deposits on the catalyst surface [5]. Maintaining this ratio allows for a reversible reaction between Ni and H₂S, as sulfur is removed from the surface through the reduction of Ni-S species by the stream of generated hydrogen [6].

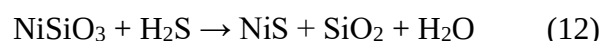
The process temperature is a key parameter influencing catalyst poisoning by sulfur-containing compounds.

It is shown in [7] that the same degree of methane conversion is observed if, all other conditions being equal, a gas containing 100 mg of sulfur per Nm³ is converted at 910°C, while a gas containing 200 mg of sulfur per Nm³ is converted at 950°C.

It is important to note that at process temperatures above 900°C, low concentrations of hydrogen sulfide exert a stabilizing effect on the activity of catalysts containing silicon oxide [8]. This is explained by the fact that at 800°C, silicon oxide reacts with water vapor to form silicic acid, which interacts with nickel to produce inactive nickel silicate (reaction 11):

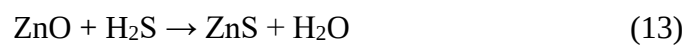


In the presence of hydrogen sulfide, nickel silicate decomposes to form nickel sulfide (reaction 12), which is subsequently reduced by hydrogen to metallic nickel:



It should be noted that during reaction 13, the surface layer can be characterized as a two-dimensional sulfide that grows on Ni sites in the form of islands with a well-defined structure.[9]

To prevent catalyst poisoning, fine purification of the feedstock is carried out at the final stage of gas feedstock preparation. This fine purification involves the absorption of residual hydrogen sulfide on zinc oxide.[10]



After the final purification stage, up to 5 ppm of hydrogen sulfide remains in the feedstock. All the aforementioned feedstock preparation stages are highly costly, and eliminating even one of them would significantly improve the economic efficiency of the hydrocarbon steam reforming process.[11]

Discussion. Taken together, the reported findings indicate that maintaining catalyst activity requires control of both sulfur exposure and carbon deposition, while high operating temperatures also increase the risk of nickel sintering. The need to reduce H_2S to about 5 ppm before reforming adds cost to feedstock preparation, which supports the manuscript's stated need for sulfur-tolerant and coke-resistant nickel-based catalysts.[12][13]

Carbon formation on catalyst surfaces is a key challenge in the hydrocarbon steam reforming process. Non-steady-state conditions during unit startup, poisoning by sulfur-containing compounds, and a low steam-to-carbon ratio are the primary causes of carbon formation.[14]

Carbon can form via three main mechanisms (Figure 2):

- formation of filamentous carbon;
- formation of encapsulated carbon;
- formation of pyrolytic carbon.

The reactions leading to carbon formation are as follows:

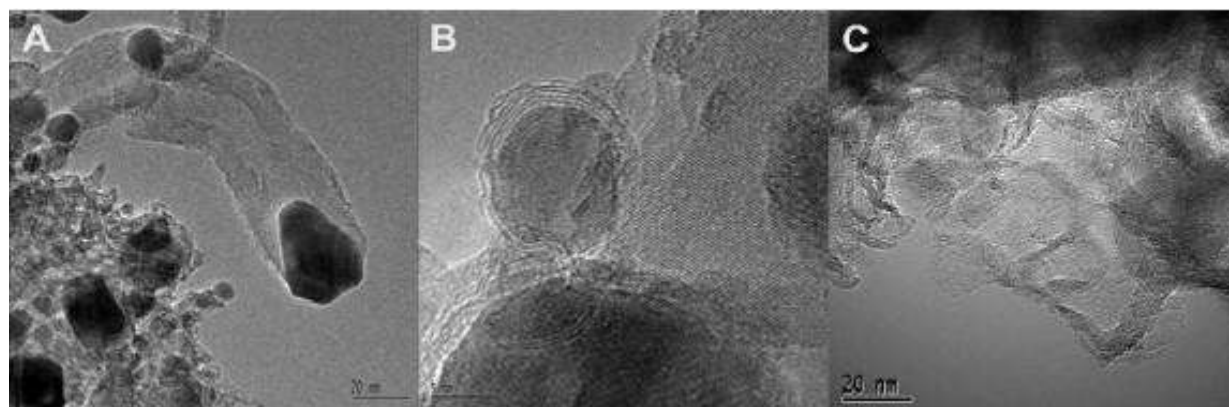
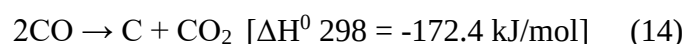


Figure 2. TEM images of carbon deposits: (a) filamentous carbon, (b) encapsulated carbon, (c) pyrolytic carbon.

The formation of filamentous carbon is the most destructive process for the catalysts. This type of carbon is highly robust; as the carbon particle grows and impinges upon the walls of the support

pores, it gradually disrupts the support's structure. This type of carbon can be characterized as long nanofilaments with Ni crystals at their tips, formed during the decomposition of CO and methane.[15]

Conclusion

For the majority of industrial catalysts used in the steam reforming process, this requirement cannot be met; hydrogen sulfide poisoning leads to a rapid loss of activity. High sensitivity to poisoning by sulfur compounds necessitates multi-stage, deep purification of natural gas to remove hydrogen sulfide, the content of which must not exceed 5 ppm. The need for such extensive purification significantly increases the cost of the process. To date, there are no effective methods for enhancing the sulfur tolerance of the most active nickel-based catalysts. In this context, one of the most pressing issues in petrochemistry is the development of the scientific foundations for synthesizing highly efficient, nickel-based catalysts that are resistant to poisoning by sulfur compounds and stable against coke formation

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