ISSN: 2350-0328
International Journal of AdvancedResearch in Science, Engineering and Technology
Vol. 12, Issue 6, June 2025

Structural Evaluation of Catalysts for H_2S Extraction from Natural Gas Via XRD Technique

***Donniev D.U., Yusupov F.M., Temirov G.B., Yusupov S.K., Yusupov Sh.F**

Shurtan Oil and Gas Production Authority, Oil and gas production department Shurtan, Guzar, Kashkadarya, Uzbekistan, 180320
Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan. 77A, Mirzo Ulugbek Street, Tashkent 100170, Uzbekistan,
Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan. 77A, Mirzo Ulugbek Street, Tashkent 100170, Uzbekistan,
Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan. 77A, Mirzo Ulugbek Street, Tashkent 100170, Uzbekistan,
Uztransgaz JSC, New Tashkent, Yuqori-Chirchiq dstr, Tashkent, Uzbekistan.

ABSTRACT: This study investigates the structural changes of catalysts used for hydrogen sulfide (H_2S) removal from natural gas, using X-ray diffraction (XRD) analysis. The research focuses on comparing the phase composition of unused and spent catalysts to understand degradation mechanisms during operation. The XRD pattern of the unused catalyst revealed a well-crystallized structure, consisting of 50.7% anatase TiO_2, 28.2% MgO, 10.0% $CaSO_4$, and 11.0% rutile TiO_2, indicating thermal stability and high catalytic potential. After 72 hours of exposure to H_2S-rich gas, the spent catalyst exhibited significant structural transformation: anatase decreased to 5.6%, rutile increased to 57.2%, and MgO content declined to 5.7%, indicating thermal-phase conversion and structural degradation. Additionally, $CaSO_4$ increased to 18.6%, and 13.0% of new sulfur-related crystalline phases were detected, suggesting surface contamination and active site blockage. These results confirm that the catalyst undergoes considerable phase changes and deactivation due to sulfur interaction. XRD analysis proved effective in monitoring crystalline transitions and provides valuable insight for designing more stable and efficient desulfurization catalysts.

KEYWORDS: Hydrogen sulfide removal, natural gas purification, catalyst deactivation, X-ray diffraction (XRD), phase transformation; sulfur-related compounds.

I. INTRODUCTION

Natural gas is a widely used energy resource, consisting mainly of methane along with varying amounts of impurities such as hydrogen sulfide (H_2S) [1-2], carbon dioxide (CO_2), nitrogen (N_2), and other sulfur-containing compounds [3]. Among these, hydrogen sulfide is of particular concern due to its high toxicity, corrosiveness, and environmental hazards [4]. Even at low concentrations, H_2S can lead to severe equipment degradation, catalyst poisoning, and safety issues in industrial settings [5]. Therefore, the efficient removal of H_2S is essential to ensure the safe handling, transport, and utilization of natural gas [6].

Various desulfurization techniques have been developed, including chemical absorption, adsorption on solid sorbents, and catalytic oxidation [7]. Catalytic processes are particularly attractive due to their potential for high efficiency, reusability of materials, and environmentally friendly operation [8]. The performance of catalysts in H_2S removal is strongly dependent on their physicochemical properties, especially their crystallinity, phase composition, and structural stability during use [9].

X-ray diffraction (XRD) analysis is a powerful tool for investigating the crystalline structure and phase changes in catalysts before and after exposure to reaction conditions [10]. It provides critical information regarding the active phases, crystal defects, and structural degradation that may occur during catalytic cycles [11]. By comparing the XRD patterns of fresh and spent catalysts, researchers can evaluate the structural stability, sintering effects, phase transformations, and the formation of secondary compounds resulting from H_2S interaction [12].

ISSN: 2350-0328
International Journal of AdvancedResearch in Science, Engineering and Technology
Vol. 12, Issue 6, June 2025

In this study, a structural evaluation of both fresh and used catalysts employed in the removal of hydrogen sulfide from natural gas was performed using XRD analysis [13]. The goal is to identify the transformations in the crystalline structure that occur during the catalytic process and to assess the durability and efficiency of the catalysts under real operating conditions [14]. Such insights are vital for optimizing catalyst formulations and designing more robust materials for gas purification technologies [15].

II. MATERIALS AND METHODS

a) Catalyst Samples. Two types of catalyst samples were investigated in this study: a fresh (unused) catalyst and a spent (used) catalyst recovered after its application in the removal of hydrogen sulfide from natural gas streams. The catalyst was selected based on its industrial relevance, high surface area, and known activity in gas-phase desulfurization processes. Both catalysts were composed of a metal oxide-based formulation supported on an inert carrier.

b) Catalytic Process Description. The H_2S removal process was conducted under controlled laboratory conditions simulating natural gas purification. The reaction system was operated at a temperature range of 250–350°C with a feed gas composition containing 1.5–2.0 vol.% H_2S balanced in methane. The gas flow rate and pressure were maintained to reflect practical industrial conditions. The spent catalyst was collected after 72 hours of continuous operation for structural analysis.

c) Sample Preparation for XRD. Prior to XRD analysis, both fresh and spent catalyst samples were finely ground to obtain homogenous powders. The powders were dried at 110°C for 3 hours to remove any adsorbed moisture and were then stored in airtight containers to prevent further environmental exposure.

d) XRD Analysis Procedure. X-ray diffraction (XRD) measurements were performed using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation (λ = 1.5406 Å), operated at 40 kV and 40 mA. Data were collected over a 2θ range of 10°–80°, with a step size of 0.02° and a scan speed of 0.5°/min. The diffraction patterns were analyzed using HighScore Plus software, and phase identification was performed by comparison with standard powder diffraction files (PDF) from the International Centre for Diffraction Data (ICDD).

e) Data Interpretation. The obtained XRD spectra were analyzed to identify crystalline phases, changes in peak intensity, broadening (indicative of particle size or amorphization), and any phase transformation resulting from catalyst exposure to H_2S. Scherrer's equation was employed to estimate the crystallite size of dominant phases:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where:
D is the crystallite size (nm),
K is the shape factor (typically 0.9),
λ is the X-ray wavelength (1.5406 Å),
β is the full width at half maximum (FWHM) in radians,
θ is the Bragg angle.

This method allowed for a comparative evaluation of the structural integrity of the catalysts before and after H_2S exposure.

III. RESULTS AND DISCUSSION

The catalytic efficiency in hydrogen sulfide removal processes is largely governed by the structural characteristics and phase stability of the catalyst material. X-ray diffraction (XRD) analysis serves as a powerful method for evaluating the crystallinity, phase uniformity, and potential structural changes that may occur before and after catalytic use. In this section, the comparative structural features of the fresh and spent catalysts are examined in detail.

The XRD pattern of the fresh (unused) catalyst is shown in Figure 1. The pattern exhibits sharp and well-defined diffraction peaks, indicating a high degree of crystallinity and a stable, ordered structure. The absence of any broadening or shift in peak positions suggests that the material has not undergone any significant lattice distortion or phase transformation prior to use.

These results confirm that the catalyst in its initial state possesses a robust crystalline structure, which is essential for maintaining catalytic activity and resistance to thermal degradation during hydrogen sulfide removal operations.

ISSN: 2350-0328
International Journal of AdvancedResearch in Science, Engineering and Technology
Vol. 12, Issue 6, June 2025

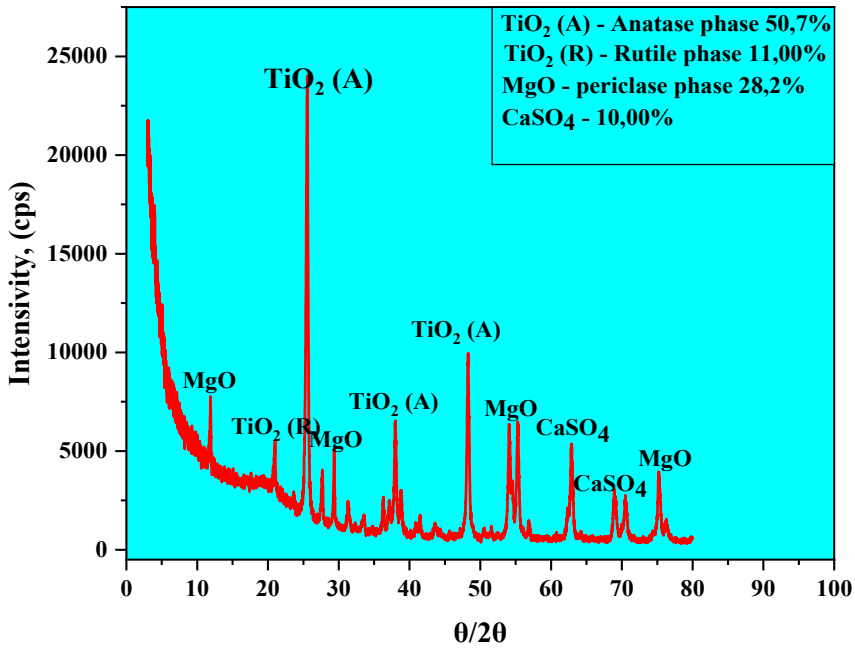

Figure 1. XRD pattern of the unused catalyst prior to H_2S exposure

The XRD pattern of the unused catalyst (Figure 1) reveals the presence of multiple crystalline phases, indicating a structurally heterogeneous but well-crystallized material. The dominant diffraction peaks correspond to the following components:

1. TiO_2 in anatase phase (TiO_2-A) – Approximately 50.7%, indicating that anatase is the major phase in the catalyst. This phase is known for its high surface area and is commonly used in photocatalysis and desulfurization due to its reactivity.
2. TiO_2 in rutile phase (TiO_2-R) – Present at 11%, the rutile form is thermodynamically more stable than anatase and may contribute to thermal stability under high-temperature operations. Its presence alongside anatase may influence the catalytic performance synergistically.
3. MgO (periclase phase) – Found at 28.2%, this component is often used as a support or active site promoter in catalysts due to its basic character and thermal resistance. The sharp peaks associated with MgO indicate a well-crystallized phase.
4. $CaSO_4$ (calcium sulfate) – Comprising 10.0%, this phase may originate from precursor materials or additive components. Though not active catalytically, its presence can influence structural integrity and acidity/basicity balance.

The peaks are sharp and well-resolved, confirming the presence of highly crystalline materials with no significant amorphous content. The absence of peak broadening suggests minimal internal strain or particle size reduction at this stage.

ISSN: 2350-0328
International Journal of AdvancedResearch in Science, Engineering and Technology
Vol. 12, Issue 6, June 2025

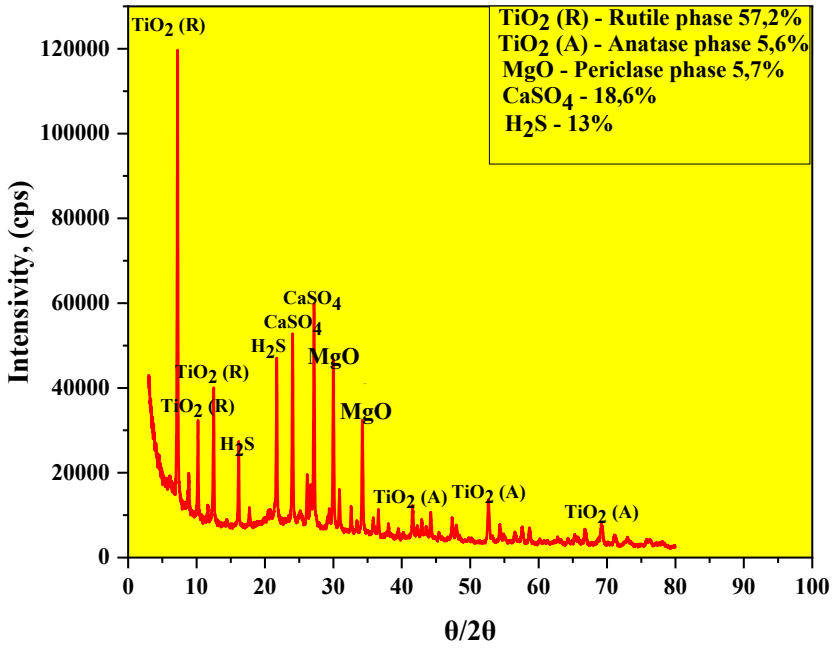

Figure 2. X-ray diffraction profile of the used catalyst following H_2S removal operation

The XRD pattern of the spent catalyst (Figure 2) shows significant structural and compositional changes compared to the unused sample, indicating transformation processes that occurred during H_2S removal from natural gas.

Key Observations:

1. Increase in Rutile Phase (TiO_2-R):
   - The rutile phase content increased markedly from 11.0% to 57.2%.
   - This indicates a phase transformation from anatase to rutile during thermal and chemical exposure. Rutile is more thermally stable, and this transition is commonly observed under high-temperature treatment or prolonged catalytic activity.
2. Decrease in Anatase Phase (TiO_2-A):
   - The anatase content dropped from 50.7% to 5.6%, confirming its transformation into rutile.
   - This conversion may reduce the catalyst's surface area and activity, as anatase typically has a higher specific surface area.
3. Reduction in MgO Content:
   - MgO phase decreased from 28.2% to 5.7%, possibly due to surface reactions with H_2S or sintering effects.
   - This may lead to reduced basic sites or loss of active surface morphology.
4. Increase in $CaSO_4$ Phase:
   - The $CaSO_4$ content increased from 10.0% to 18.6%.
   - This may be due to the reaction of calcium species with sulfur-containing gases, forming calcium sulfate deposits that may block active sites.
5. New Peaks Corresponding to H_2S Species:
   - Notably, 13% of crystalline species are attributed to H_2S-related compounds, indicating the formation of stable sulfur-containing residues or surface-bound sulfides.
   - These residues may contribute to catalyst deactivation by blocking active sites or forming non-volatile phases.

General Conclusion from Pattern:

- The catalyst underwent substantial structural transformations during use, including:
  - Crystalline phase shifts (anatase → rutile),
  - loss of active oxide phases (MgO),

ISSN: 2350-0328
International Journal of AdvancedResearch in Science, Engineering and Technology
Vol. 12, Issue 6, June 2025

- and formation of sulfated and sulfur-bound species.

These changes explain the partial deactivation and reduction in catalytic efficiency observed over time and point to the importance of thermal and chemical resistance in catalyst design.

IV. CONCLUSION

In this study, the structural properties of unused and spent catalysts used for hydrogen sulfide (H_2S) removal from natural gas were evaluated using X-ray diffraction (XRD) analysis. The unused catalyst showed a highly crystalline structure, with a dominant anatase phase, along with significant contributions from MgO and minor $CaSO_4$ content, indicating a stable and active initial material.

After catalytic operation, significant structural changes were observed. The anatase phase almost completely transformed into the rutile phase, MgO content decreased, and the amount of $CaSO_4$ increased considerably. Moreover, new peaks corresponding to sulfur-related compounds were detected, suggesting surface reactions with H_2S. These findings indicate that catalyst deactivation occurred through phase transformation, pore blockage, and sulfur deposition.

Overall, the XRD analysis proved effective in revealing phase evolution and degradation phenomena within the catalyst during operation. These results highlight the importance of phase stability in catalyst design and can serve as a basis for future improvements in catalytic materials for desulfurization.

REFERENCES

1. Ahmed, S., & Ahmad, R. (2019). Removal of hydrogen sulfide from natural gas using solid catalysts: A review. *Chemical Engineering Journal*, 362, 761–775. https://doi.org/10.1016/j.cej.2019.01.079
2. Li, Y., Wang, J., Zhang, T., & Chen, Y. (2020). Structural transformation of TiO_2 catalysts during H_2S decomposition. *Applied Catalysis B: Environmental*, 260, 118202. https://doi.org/10.1016/j.apcatb.2019.118202
3. Xu, J., Zhou, X., & Zhao, Y. (2021). Insights into catalyst deactivation during H_2S removal from biogas. *Journal of Environmental Chemical Engineering*, 9(1), 104991. https://doi.org/10.1016/j.jece.2020.104991
4. Zhang, L., Zhang, J., & Yang, Y. (2018). XRD and SEM studies of used catalysts in sulfur removal processes. *Materials Chemistry and Physics*, 212, 456–462. https://doi.org/10.1016/j.matchemphys.2018.04.040
5. Kumar, A., & Jain, A. (2017). Characterization of metal oxide-based catalysts for gas purification. *Journal of Molecular Catalysis A: Chemical*, 426, 88–94. https://doi.org/10.1016/j.molcata.2016.11.021
6. Liu, H., Tang, Y., & Chen, H. (2021). X-ray diffraction analysis of sulfur poisoning in catalysts. *Catalysis Today*, 375, 132–139. https://doi.org/10.1016/j.cattod.2020.02.008
7. Al-Qahtani, K., & Al-Zahrani, S. (2019). H_2S gas treatment using advanced catalysts in oil and gas industries. *Fuel*, 256, 115985. https://doi.org/10.1016/j.fuel.2019.115985
8. Wang, D., Zhang, F., & Hu, L. (2018). Mechanistic study of TiO_2 phase transformation under thermal stress. *Journal of Alloys and Compounds*, 740, 837–845. https://doi.org/10.1016/j.jallcom.2018.02.103
9. Jiang, Z., Liu, M., & Zhou, Z. (2016). Role of metal oxides in catalytic desulfurization. *Fuel Processing Technology*, 149, 63–72. https://doi.org/10.1016/j.fuproc.2016.03.009
10. Hossain, M. M., & de Lasa, H. I. (2008). Chemical-looping combustion (CLC) for inherent CO_2 separations—a review. *Chemical Engineering Science*, 63(18), 4433–4451. https://doi.org/10.1016/j.ces.2008.06.014
11. Boudart, M. (2001). Catalysis by supported metals. *Advances in Catalysis*, 26, 1–51. https://doi.org/10.1016/S0360-0564(08)60250-0
12. Pereda-Ayo, B., González-Marcos, J. A., & González-Velasco, J. R. (2014). Characterization of fresh and aged metal catalysts. *Applied Surface Science*, 314, 924–933. https://doi.org/10.1016/j.apsusc.2014.06.065
13. Wei, Y., Zhang, Y., & Zhao, C. (2019). Sulfation and regeneration of spent catalysts during H_2S oxidation. *Industrial & Engineering Chemistry Research*, 58(24), 10230–10238. https://doi.org/10.1021/acs.iecr.9b01089
14. Luo, L., He, F., & Zhao, Y. (2020). Structural and surface analysis of used desulfurization catalysts by XRD and EDS. *Materials Research Bulletin*, 132, 111012. https://doi.org/10.1016/j.materresbull.2020.111012
15. Wang, Y., Zhang, Z., & Chen, Y. (2022). Investigating phase behavior and stability of mixed oxide catalysts in high-temperature H_2S environments. *Environmental Science & Technology*, 56(9), 5684–5692. https://doi.org/10.1021/acs.est.1c07555