



REPUBLIC OF TURKEY
UNIVERSITY OF YALOVA
INSTITUTE OF GRADUATE STUDIES

**DEVELOPMENT OF ZINC TITANATE-BASED H₂S ADSORBENTS FOR
BIOMASS GASIFICATION PROCESS**

DISSERTATION
Özlem TUNA
165307001

Department of Chemical Engineering
Chemical and Process Engineering Programme

Advisor: Assoc. Prof. Dr. Esra BİLGİN ŞİMŞEK
Co-Advisor: Assoc. Prof. Dr. Alper SARIOĞLAN

FEBRUARY 2021



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Özlem TUNA, a **Ph.D.** student of University of YALOVA Institute of Graduate Studies with student ID number **165307001**, defended the **dissertation** entitled **“DEVELOPMENT OF ZINC TITANATE-BASED H₂S ADSORBENTS FOR BIOMASS GASIFICATION PROCESS”**, which he/she prepared after fulfilling the requirements specified in the associated legislations, in front of the jury whose signatures are below and was found to be successful with unanimity/majority.

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PREFACE

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Özlem Tuna



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ABBREVIATIONS

ATR	: Attenuated Total Reflectance Method
BET	: Brunauer-Emmett-Teller
BFB	: Bubbling Fluidized Bed
CFB	: Circulating Fluidized Bed
CF	: Ceramic Filter
CN/TS	: Core Network/ Technical Specification
Cu-ZT	: Copper-doped Zinc Titanate
d-CF	: Disc Ceramic Filter
EDX	: Energy-Dispersive X-ray
FID	: Flame Ionization Detector
FTIR	: Fourier-transfer infrared
GC	: Gas Chromatography
JCPDS	: The Joint Committee on Powder Diffraction Standards
MW_{th}	: Megawatt Thermal
PID	: Proportional–Integral–Derivative
p-CF	: Powder Ceramic Filter
ppmv	: Parts Per Million Volume
SEM	: Scanning Electron Microscopy
TEM	: Transmission Electron Microscopy
TCD	: Thermal Conductivity Detector
UV	: Proportional–Integral–Derivative
WGS	: Water-Gas Shift Reaction
XRD	: X-Ray Powder Diffraction
XPS	: X-Ray Photoelectron Spectroscopy
ZT	: Zinc Titanate



SYMBOLS

a	: Reaction rate at certain time (t) (mol/ L min)
a₀	: Reaction rate on a solid (mol/ L min)
c	: BET constant
C	: Hydrogen sulfur outlet concentration (ppmv)
C₀	: Hydrogen sulfur inlet concentration (ppmv)
E₁	: Adsorption heat for first layer (J)
E_C	: Condensation heat (J)
F	: Volumetric gas flow rate (L/min)
H₂S_{in}	: Inlet hydrogen sulfur concentration (ppmv)
H₂S_{out}	: Outlet hydrogen sulfur concentration (ppmv)
Inlet_{C₆H₆}	: Inlet benzene concentration (g benzene/ g total solution)
k_d	: Deactivation rate constant (/min)
k (k_c)	: Initial adsorption rate constant (L/g min)
N	: Avogadro's number
Outlet_{C₆H₆}	: Outlet benzene concentration (g benzene/ g total solution)
P	: Equilibrium pressure (bar)
P₀	: Saturation pressure (bar)
R	: Ideal gas constant (J/Kmol)
S_{total}	: Total surface area (m ²)
S_{BET}	: Specific surface area (m ²)
s	: Adsorption cross-section
T	: Temperature (°C)
t	: Adsorption time (min)
v	: Adsorbed gas quantity
v_m	: Monolayer adsorbed gas quantity
V_{in}	: Inlet methane concentration as volumetric percentages (%)
V_{out}	: Outlet methane concentration as volumetric percentages (%)
W	: Adsorbent amount (g)
%X_i	: Hydrogen sulfur conversion value
%CH₄	: Percentage of methane amount
%C₆H₆	: Percentage of benzene amount



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DEVELOPMENT OF ZINC TITANATE-BASED H₂S ADSORBENTS FOR BIOMASS GASIFICATION PROCESS

ABSTRACT

The goal of this research study is to develop copper promoted zinc titanate based adsorbents and examine H₂S elimination during biomass gasification process by combining desulfurization and reforming stages. Firstly, the effects of fluid velocity and temperature on the desulfurization of Zn₂TiO₄ (ZT) were investigated to determine mass transfer limitation. The tests with different gas flow rates suggested that surface-reaction controlled the mechanism; while the reaction rates at high temperatures were found greater resulting high diffusion coefficient. The relationship was supported with TEM analysis, demonstrating that high temperature enabled formation of small ZnS particles which suppressed product layer resistance. Under both steam and H₂ atmospheres, the efficiency of ZT sample was reduced due to the steam poisoning of active sites, thereby the activity was decreased. In the second part, copper doped zinc titanate (Cu-ZT) adsorbents with different Cu/Zn weight ratios were prepared with co-precipitation method and the properties of the samples were investigated by XRD, XPS, BET and SEM/EDS analyses. XPS analysis revealed that the successful addition of Cu into the main lattice which was confirmed by presence of Cu2p_{3/2} state and oxygen peaks with high-intensity. The doping with Cu significantly affected the desulfurization efficiency especially under H₂ atmosphere; which H₂S removal of bare ZT was almost zero, while Cu-ZT adsorbent exhibited approximately 60% removal after 5 h. In the last part; different amounts of Cu-ZT adsorbents were incorporated with CaSiO₃ based filter via ball-milling process to integrate as a protective layer for Ni/Al₂O₃ impregnated filter during hydrocarbon reforming. The characterization with XRD, SEM and FTIR techniques indicated that Cu-ZT grains were homogeneously distributed on the host lattice of ceramic filter. The incorporation of Cu-ZT into the filter structure remarkably enhanced the sulfur resistance under reducing and gasification atmospheres which were attributed to the increasing affinity and preventing diffusion limitation. Although, the CH₄ and C₆H₆ reforming activities of Ni/Al₂O₃ based catalytic filter decreased in the presence of H₂S, the performance was improved by integrating with the Cu-ZT/filter sample as primarily active stage in the integrated process. The hybrid process displayed superior reforming efficiencies for CH₄ and C₆H₆ degradation in the H₂S atmosphere, which were 10 times higher for methane and 1.15 times higher for benzene than that of the single stage system. Herein, an innovative concept was found to obtain high quality synthesis gas by integrating desulfurization and reforming processes.

Key Words: Zinc titanate, desulfurization, methane reforming, integrated gasification system



BİYOKÜTLE GAZLAŞTIRMA İŞLEMİ İÇİN ÇİNKO TİTANAT ESASLI H₂S ADSORBENTLERİNİN GELİŞTİRİLMESİ

ÖZET

Bu çalışmanın amacı, bakır katkılı çinko titanat esaslı adsorbanların geliştirilmesi ve biyokütle gazlaştırma prosesi sırasında entegre sistemde H₂S gideriminde kullanımının incelenmesidir. İlk olarak; Zn₂TiO₄ (ZT) adsorbanı ile gaz akış hızı ve sıcaklığın kükürt giderim performansına etkisi incelenerek kütle transfer hız sınırlayıcı basamakları belirlenmiştir. Farklı akışkan hızında gerçekleştirilen deney sonuçlarına göre, söz konusu kükürt gideriminin yüzey reaksiyonu ile kontrol edildiği; reaksiyon hız sabitlerinin sıcaklık ile artarak yüksek difüzyon katsayılarının elde edildiği gözlemlenmiştir. Sıcaklık ve reaksiyon hızı arasındaki ilişki TEM analizi ile desteklenmiş; yüksek sıcaklıklarda daha küçük boyutlu ZnS partiküllerinin oluşmasıyla ürün tabaka direncinin etkisi azalmıştır. Hidrojen ve su buharı varlığında, ZT numunesinin etkinliğinin aktif yapıların zehirlenmesinden dolayı azaldığı gözlenmiştir. İkinci aşamada; ağırlıkça farklı Cu/Zn oranlarında bakır katkılı çinko titanat (Cu-ZT) adsorbanları çöktürme metodu ile hazırlanmış ve malzemelerin özellikleri XRD, XPS, BET ve SEM / EDS analiz yöntemleri ile araştırılmıştır. XPS analiz sonuçlarında Cu2p_{3/2} spektrumu ve daha keskin oksijen piklerinin gözlenmesiyle bakırın çinko titanat yapısının içerisine başarıyla eklendiği sonucuna varılmıştır. Bakırın özellikle hidrojen ortamında sülfür giderim aktivitesi üzerine etkisinin belirgin olduğu; saf ZT numunesinin kükürt tutma kapasitesi neredeyse yok iken, Cu-ZT adsorbanı 5 saatin sonunda %60 giderim göstermiştir. Son aşamada, Cu-ZT yapısı farklı oranlarda CaSiO₃ esaslı filtre yapısı içerisine bilyeli öğütme işlemi ile katılmıştır. XRD, SEM ve FTIR karakterizasyon sonuçlarına göre; Cu-ZT taneciklerinin homojen şekilde filtre yapısına dağıldığı gözlemlenmiştir. Ayrıca, Cu-ZT içeren filtre yapıları indirgeyici ve gazlaştırma ortamlarında kayda değer kükürt tutma aktivitesi göstermişlerdir ve bu aktivitelerin Cu-ZT oranı ile arttığı gözlenmiştir. Diğer yandan, Ni/Al₂O₃ esaslı katalitik filtrenin, H₂S varlığındaki metan ve benzen parçalama aktivitesinin düştüğü gözlenmiştir. Bu Cu-ZT destekli filtre bazlı malzemeler, Ni/Al₂O₃ emdirilmiş filtreyi H₂S'den korumak için öncelikli filtre katmanı olarak kullanılmıştır. Böylece, iki filtre yapısı içeren entegre sistem ile metan ve benzen reform etkinlikleri tek-aşamalı sisteme göre yaklaşık metan için 10 kat ve benzen için 1,15 kat artarak yükselmiştir. Kükürt giderim ve reformlama proseslerinin entegre edilmesiyle yüksek kalitede sentez gazı elde etmek için yenilikçi bir ünitesi tasarlanmıştır.

Anahtar Kelimeler: Çinko titanat, kükürt giderme, metan dönüştürme, entegre gazlaştırma sistemi



1. INTRODUCTION

Current energy consumption and growing population have compelled researchers to look for alternative resources. The environmental pollution issues of traditional fossil energy sources have led to explore sustainable and renewable approaches for green energy production. Biomass is comprised of organic matters existing in the biosphere derives from lignocellulosic compounds in plant and animal origins. The utilization of these abundant and low cost organic materials has potential to manage the crises of waste disposal. Thus, biomass has been considered as a promising energy since it also minimizes CO₂ release. The advantages of biomass utilization in renewable energy are summarized in Figure 1.1

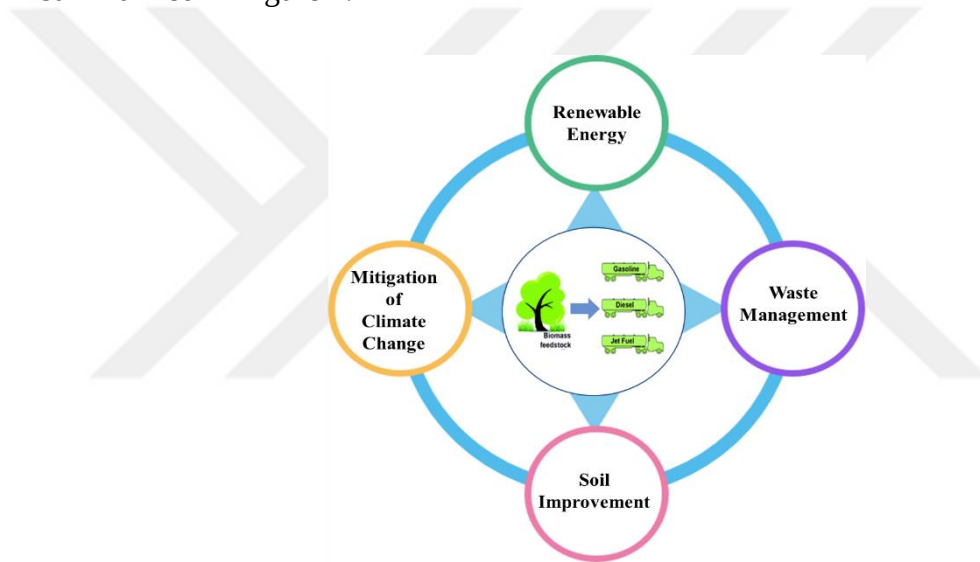


Figure 1.1: Schematic representation of advantages in biomass utilization

Biomass is transformed to gaseous and liquid fuels through thermo-chemical and biochemical processes (Figure 1.2). The biological methods can be applied on limited feedstocks, while the utilization on range of the thermo-based approaches is remarkably high. In terms of thermo-chemical conversion pathways, gasification represents the most attractive method due to higher degradation efficiency and long-term resistant of equipment. In this technology, biomass is reformed into synthesis gas which consists of a relatively high content of methane and hydrogen. The resultant gas product has numerous application areas, namely power generation, fuels, and basic chemicals manufacturing. However, impurities (fly ash & particulates) and inevitable by-products (tar ammonia, sulfur etc.) can bring a bunch of challenges to its direct

utilization. Tar formation is the major problem which greatly influences the quality of the synthesis gas by blocking the equipments with heavy hydrocarbons. Although effective tar destruction techniques have been extensively intensified with nickel catalysts in literature, the elimination of sulfur compounds still constitutes a major problem [1]. During biomass gasification, almost 95% of the sulfur content in biomass releases as hydrogen sulfur (H_2S), decreasing the total efficiency of the process owing to the poisoning of catalytic active sites and the corrosion of metallic equipments [2] .

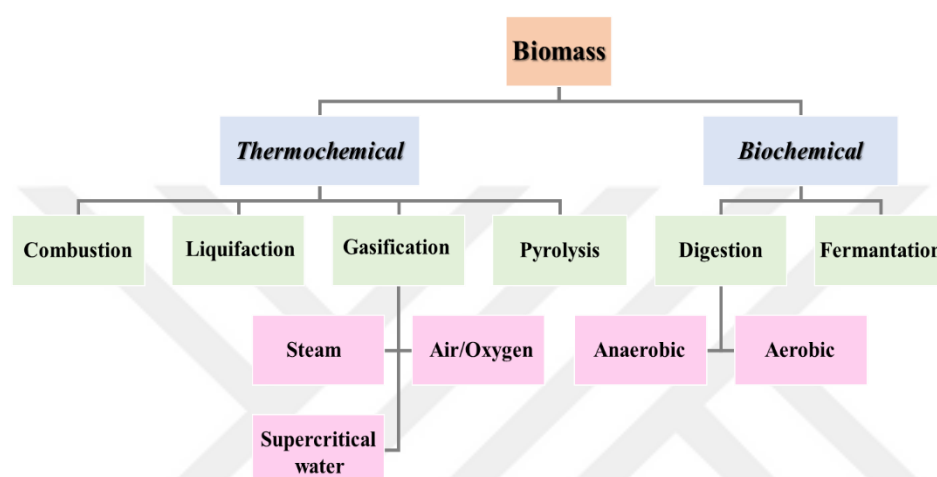


Figure 1.2: Thermochemical and biochemical biomass conversion routes

The removal of H_2S (desulfurization) can be performed via three main methods: (i) adsorption (dry desulphurization over solid sorbents), (ii) absorption (scrubbing with chemical agents) and (iii) conversion (i.e. selective catalytic oxidation or Claus process) [3]. Adsorptive desulfurization has been emerged as a low-cost alternative technique performed with sulfidation over metal oxide based adsorbents [4]. Several potential candidates (i.e., iron, zinc, calcium, cobalt, copper) can be established for the desulfurization process [4]. The chemisorption of sulfur on zinc-based surfaces can be considered as an ideal approach due to the excellent affinity of metal towards H_2S [5]. However, the utilization of zinc oxide (ZnO) adsorbents is restricted to temperatures higher than $550\text{ }^{\circ}C$ because of the formation of zinc vapor, thus it can be used only if it is incorporated with other metal oxides such as Fe_2O_3 and TiO_2 , increasing the stability and efficiency [6, 7]. Therefore, zinc titanates can be regarded as feasible adsorbents in the desulfurization process.

In terms of sufficient biomass gasification, the development of advanced concepts has been highlighted by combining biomass reforming and gas cleaning in one unit in order to obtain in situ removal of tar and sulfur [8]. Thus, the construction of hybrid systems including catalytic gasifier and absorber can provide high-quality synthesis gas as a product. Nickel based catalytic filters inserted in the freeboard of gasifier can be effectively applied in these integrated systems, thereby the deactivation of Ni sites with sulfur is prevented [9, 10]. Therefore, in this thesis, efforts were made to develop zinc titanate structures as a protective layer towards H_2S and to hinder the poisoning of Ni active sites on the catalytic structure.

1.1 Research Objectives

In this research, three main steps were designed to achieve successful desulfurization during tar degradation. The research stages can be detailed, as follows:

- ❖ **I. Sub-phase:** Zinc orthotitanate (Zn_2TiO_4) as a promising sulfur adsorbent, was evaluated in desulfurization process. The influence of mass transfer limitations on the desulfurization activity was investigated in detail by varying experimental conditions followed by characterization methods, namely XRD, SEM/EDS and TEM. In addition, the performance of the zinc-based adsorbents was examined in different gas mixtures.
- ❖ **II. Sub-phase:** The effect of dopant on the desulfurization performance of zinc titanate was examined. For that, copper was utilized as an additive to facilitate the adsorption rate of zinc titanate with different copper amount. Furthermore, the effects of Cu content on the structural and morphological properties of Zn_2TiO_4 were explored by using characterization techniques of XRD, XPS, SEM and BET. To quantify the relative share of the as-obtained adsorbent, the activity was also evaluated by considering H_2S removal ratio in reducing, oxidizing and synthesis gas atmospheres.
- ❖ **III. Sub-phase:** An integrated adsorptive-catalytic system was proposed as an advanced biomass gasification technology in which tar reforming with being less affected by sulfur. The integrated system consisted of two units which

were developed to achieve desulfurization followed by hydrocarbon cracking. For that, two kinds of materials, namely $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{Zn}_2\text{TiO}_4$ were incorporated with ceramic filter through impregnation and ball-milling methods, respectively. Primarily, the H_2S removal driven by adsorption was evaluated in different environments in terms of the structure including zinc titanate. Then, $\text{Ni}/\text{Al}_2\text{O}_3$ based catalytic filter was performed in methane and benzene degradation in simulated sulfur-free and sulfur-included gasification environments. Finally, both active materials were performed in series to evaluate the efficiency of the integrated system.



2. BIOMASS GASIFICATION

Gasification has been presented as a promising technology for sustainable and clean energy production. Biomass gasification is a thermochemical technique to convert carbonaceous materials into combustible gaseous mixture by using gasifying agent at high temperatures. The combustible gaseous mixture is mostly known as synthesis or producer gas. The producer gas mainly consists of carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), methane (CH₄), trace amounts of higher hydrocarbons (ethene, ethane), water, nitrogen (with air as oxidant) and various contaminants, such as small char particles, ash, tars, higher hydrocarbons, and oils. The composition of the producer gas can be changed by gasification temperature and varying oxidizing agents (oxygen/air and steam). The oxygen provides a producer gas to include low hydrogen content and higher amount of carbon-based gas components (mainly CO and CO₂). If low amount of oxygen is used, the producer gas involves CO, while the gas mixture includes CO₂ in terms of higher oxygen. Moreover, when the amount of oxygen exceeds stoichiometric amount, the gasification process tends to combustion, resulting decreased heating value of the as-obtained gas product. In case of steam, the ratio of hydrogen to carbon is high, resulting hydrogen-rich synthesis gas, which is the most promising product for further evaluation [11-13].

The physical, chemical, and thermal processes occurred during biomass gasification process can be listed as drying, pyrolysis, combustion, and gasification. Although the steps are generally modelled in series, the boundary between them is not sharp, which is attributed to the overlapping of the stages during gasification process. Figure 2.1 depicts a schematic representation of the gasification steps. The four stages are described, as follows [14, 15]:

- ❖ In drying (dehydration step), biomass losses its moisture content below 125 °C, which is necessary to obtain the gas product with high heating value.
- ❖ In pyrolysis step (devolatilization), biomass is decomposed to a carbon-rich effluent including solid and volatiles via a series of complex reactions at temperature ranges from 350 °C to 700 °C. The volatiles consist of two different parts: non-condensable and condensable gases. The non-condensable gases mostly include H₂, CH₄, CO, CO₂, H₂O, N₂, O₂; while the condensable

part is comprised of tar and water. In addition, solid part includes char and ash. The main reaction can be summarized as follow:

Biomass $\rightarrow$ gases(CO, CO₂, H₂, CH₄, N₂...) + char + tar + water

- ❖ In combustion, required thermal energy for endothermic reactions in pyrolysis and gasification is supplied via oxidation of the char. On the other hand, the heat may be indirectly supplied from the combustion of some starting material or char followed by transfer of synthesis gas to the gasifier.

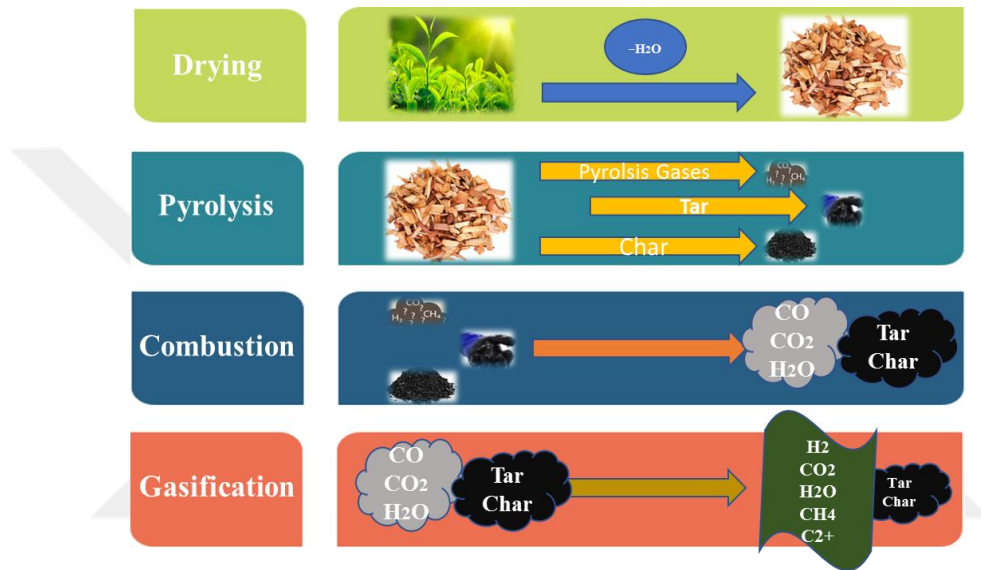
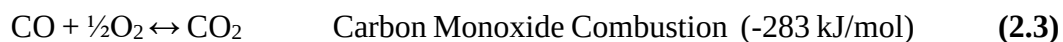
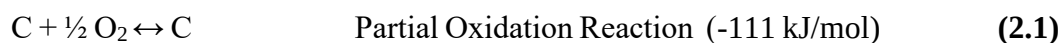


Figure 2.1: Schematic representation of biomass gasification steps

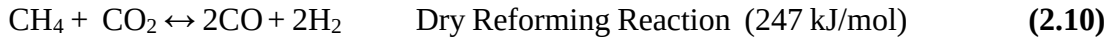
- ❖ In gasification (reduction), lots of chemical reactions occur and the reactions can be categorized in three sections: combustion reactions, homogeneous reaction (Water Gas Shift Reaction, Steam Reforming, Dry (CO₂) Reforming) and heterogeneous reactions (Boudourd Reaction, Water Gas Reaction and Methanation). In addition, tar-reforming, a secondary thermal cracking, can be added in this stage. The most dominant reactions are mentioned as follows [16]:

➤ **Combustion reactions:**





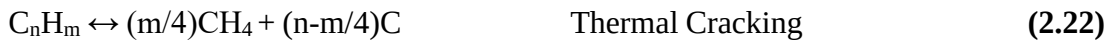
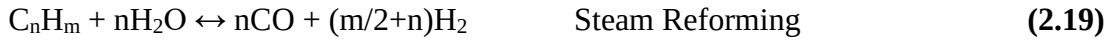
➤ **Homogeneous gasification reactions:**



➤ **Heterogeneous gasification reactions:**



➤ **Tar reactions:**



In biomass gasification, carbon, which is considered as primary source of biomass, reacts with a reactive gas (either carbon dioxide or steam) at elevated temperature. The cracking stage is mainly dominated with carbon steam reactions (Eq. (2.14-15)) and Boudouard reaction (Eq. 2.16), which can be used to illustrate the basic principles of

thermal gasification process. These reactions are endothermic and, therefore, require heat and elevated temperatures to occur at reasonable rates. The heat is supplied with exothermic combustion reactions (Eq. (2.1-6)) which take place in conjunction with the reduction gasification reactions. Furthermore, the homogeneous oxidation reactions promote the existence of excess active gas components in the gasification environment. Another reaction groups that have to be considered are homogeneous gasification reactions, which are attributed to water-gas shift reaction, reforming reactions and methanation (Eq. (2.7-13)). The gas-phase reactions are important for modifying the composition of the producer gas. The reforming reactions mainly provides the decomposition of the aromatic hydrocarbons (tar) to smaller molecules including low carbon numbers (Eq. (2.18-22)). The methane reforming reactions (Eq. (2.8-10)) are generally considered as the consecutive steps for tar degradation reactions. The methane cracking reactions are essential routes for syngas production with high-qualified. However, a large amount of energy is necessary due to their endothermic kinetics. Meanwhile, the water-gas shift reaction (WGS) transforms toxic CO to CO₂ and increases the H₂-amount (Eq. (2.7)), also this reaction is also used in post gasification treatment to adjust the H₂/CO ratio of the gas mixture. That is, the reaction can be considered as an another of the most important reactions during gasification process, as it enhances the quality of the producer gas, resulting from low selectivity and yield for CO. Due to the fact that the WGS reaction is moderately exothermic, the equilibrium constant decreases with temperature, and high conversions are favored by low temperatures. In addition, the methanation reactions (Eq. (2.11-13)) convert any residual carbon oxides to methane and water, consuming hydrogen, and are thus not the preferred reaction pathways. Thus, the performance of the gasification process can be greatly enhanced in the presence of suitable catalysts which promote reforming reactions under low temperature and provide the selectively formation of WGS.

2.1 Biomass Gasification Technologies

2.1.1 Traditional Technologies

Various technologies are employed for gasification of biomass. The classification of the processes can be carried out according to the type of heat supply (I), gasification agent (II), gasifier (III), and the presence of pressure (IV) as follows:

I. Classification: Autothermal or Allothermal gasification

II. Classification: Air, Oxygen and/or Steam gasification

III. Classification: Entrained bed, Fixed bed, or Fluidized bed systems

IV. Classification: Atmospheric or Pressurized gasification

The most common gasification categories are known as I. and III. classifications. One of the most essential point is the source of required heat to endothermic gasification reactions to determine gasification manner. Two different sources can be considered, resulting two biomass gasification methods: Autothermal and Allothermal techniques. In case of autothermal (direct) gasification, the heat energy is provided by exothermic reactions taking place in situ with the gasification reactions. The exothermic reactions are assigned to the oxidation of carbon in biomass. In the Allothermal method, the heat is provided by external source, such as combustion system. Considering the energy efficiency, autothermal gasification processes have been addressed to design industrial biomass gasification [17].

In terms of gasifier type, the aspects that play an important role on the reactor design are scale of operation, feedstock flexibility, sensitivity to amount of ash and tar yield. Based on these features, three main reactor designs have been presented, as follows: fixed bed, fluidized bed, and entrained bed gasifiers. A schematic overview of the different gasifiers is depicted in Figure 2.2.

2.1.1.1 Fixed bed gasifiers

Fixed bed gasifiers are subdivided into downdraft (cocurrent) and updraft (countercurrent) systems which are based on changing the direction of gas stream and bed movement. The gasifiers require biomass particles with small size (1-3 cm) to ensure an unblocked passage of gas through the bed, resulting pellets or briquettes feedstocks. The gasification takes place in a fixed bed, in which the different gasification reactions occur in different zones. In both reactors carboneous fuel is fed from the top of the gasifier. The gasification agent enters from the bottom of updraft or the middle of downdraft gasifier, resulting a different order of reaction zones (Figure 2.2). This counterflow regime results in high amount of tars ($10\text{-}150\text{ g/m}_N^3$) and particles ($0.1\text{-}3\text{ g/m}_N^3$) in synthesis gas, while the cocurrent flow provides relatively low tar content due to the movement of pyrolysis gases through oxidation zone.

In addition, the reactors are utilized in small-scale operation of up to several MW_{th}. [12, 13].

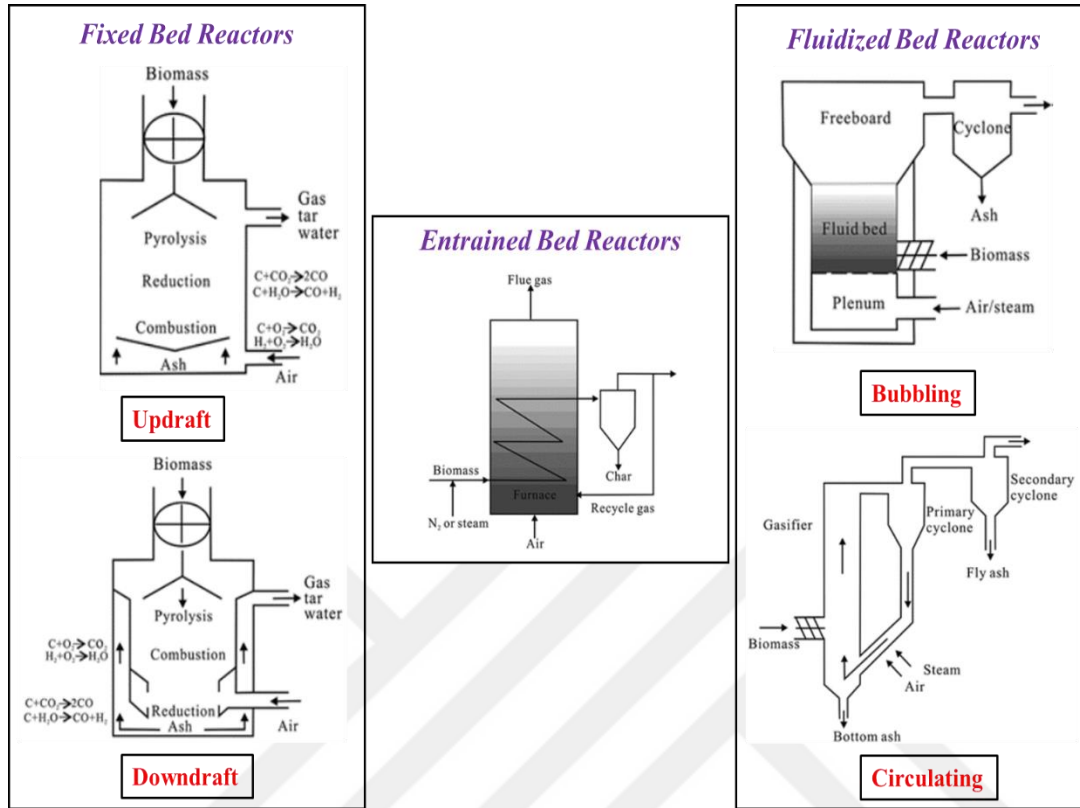


Figure 2.2: Schematic representation of different gasifiers [18]

2.1.1.2 Fluidized bed gasifiers

In fluidized bed reactor, biomass is mixed with bed materials and fluidized by the gasification agent. This type of gasifier can be utilized for variable biomass particle size and shows higher tolerance for biomass contents such as moisture and alkali metals. Due to their geometry and excellent mixing properties, the fluidized bed provides uniform temperature profile and they display high energy capacity of more than 100 MW_{th}. Furthermore, this type of reactors is mainly categorized into two groups: bubbling fluidized bed (BFB) and circulating fluidized bed (CFB). The entrained particles are removed from the process in BFB system, whereas the particles are recirculated in CFB process. The fluidized bed configurations can be utilized for large scale biomass gasification due to higher conversion tendency, improved heat and mass transfer and low tar formation. [14, 19, 20].

2.1.1.3 Entrained flow gasifiers

Entrained flow gasifiers convert the mixture of biomass and oxygen into a turbulent dust flame at high temperature and pressure within a very short period. In the gasifier, pulverized solid (particle size below 1 mm) or liquid (e.g. pyrolysis oil) can be used as a feedstock. Due to high temperatures and rapid heating, all hydrocarbons are degraded, resulting tar-free producer gas. Since the combustion stage is much slower than the pyrolysis/gasification step, the reactor has to be designed in which sufficient residence time for the complete oxidation. Furthermore, ash must be molten through the entire reactor to prevent fouling and disruptions in heat and mass flow. However, for ash rich biomass the fluidization requirements can be difficult to achieve an efficient temperature control and the usage of those gasifiers is limited in biomass gasification [21].

2.1.2 Issues in Traditional Biomass Technologies

Traditional biomass gasification technologies have been focused on process optimization by varying operational parameters such as heat management, mixing, biomass flow, feeding flexibility and residence time. The gasification techniques are aimed to obtain higher conversion of biomass and produce hydrogen-rich synthesis gas. However, the existing producer gas should undergo several treatments for subsequent use, since it has undesired components such as particulates, tar, sulphur [15]. Therefore, studies have been focused on gas cleanup technologies.

One of the most essential impurity is particulates that are solid-phase materials entrained in the as-synthesized gas stream. Particulates can be defined in two parts: inorganic part (ash) and organic part (char). The high particulate loadings in the turbulent flow gasifiers can cause clogging pipeline system and exceeding emission limits for fly-ash. The other major impurity is tar which is a mixture of black, viscous, and corrosive aromatic constituents and complex polyaromatic hydrocarbons. The presence of tar induces high oxygen and water contents, resulting in lower quality of the synthesis gas. On the other hand, the tar brings out some drawbacks on the process efficiency such as blockage and corrosion of equipment and damaging filter. Hence, the gas cleaning processes have been mainly focused on the removal of particulates and tar contaminants.

Traditional removal approaches for the matters are categorized as wet-cleaning, and dry-cleaning system, which are assigned to mechanical/physical separation methods. In wet-cleaning system, the separation is performed under 20-100 °C in wet cyclones, scrubbers or electrostatic precipitators. The cyclone, which is driven by centrifugal forces, can effectively remove particulates above about 5 µm in a diameter. However, they are not very effective in tar removal because of the tar's stickiness. In electrostatic precipitators, the particulates imparted with an electric charge are collected on scrubber plate followed by mechanically cleaning, but tar still needs further cleaning by washing. In addition, the capital cost of this method is relatively high. The other equipment, wet scrubbers collect the particulates and tar components in liquid droplets by collision [14]. Even though it is an efficient system, it consumes more energy and the tar drops tend to fouling the equipment by agglomeration. Dry gas cleaning is based on removal of the tar and particulates by a fabric filter which takes place below 200 °C. However, tar deposited on the filters cannot be easily cleaned due to condensation problem of the tar with decreased temperature [22]. Based on the drawbacks mentioned above, current interest has been to intensify the traditional methods for utilization in large-scale applications.

2.1.3 Advanced Technologies

In the concept of advanced gasification process, the integration of fluidized bed gasifiers with hot gas cleaning is the most common approach, providing effective tar conversion, thus retaining chemical energy in the product gas and increasing thermal efficiency in the whole process. In this process, the removal of tar can be completed by reactions, namely steam & dry reforming, cracking and hydro-cracking reactions (Eq. (2.17-20)). Steam reforming has been considered as the most appropriate route to tar elimination, providing tar degradation at lower temperature in the presence of catalysts. The catalytic treatment is mainly divided into two categorizes; primary treatment: within gasifier and secondary treatment: downstream of gasifier.

2.1.3.1 Primary catalytic treatment: within gasifier

In primary in-situ method, low-cost minerals such as dolomite, limestone, and olivine are used as catalysts in the gasifier. Dolomite ((Ca,Mg)CO₃) is an attractive material on account of its efficient tar removal capacity and cost effectiveness. Olivine ((Mg,Fe)₂SiO₄) and limestone (CaCO₃) can overcome the attrition problem of the

dolomite and gain opportunity to be utilized in industrial scale gasification processes. In addition, fly ash which is the main solid waste has been utilized as a catalyst due to its alkali metal content [12]. Commercial nickel catalysts have also gained significant attention to increase the efficiency of tar reforming [23-25]. Their high hydrogenation activity enables the breaking of O-H, -CH₂, -C-C-, -and -CH₃ bonds [26]. However, it shows limited performance for water gas-shift reaction and Boudouard reaction or the decomposition, resulting in low H₂ content in syngas and higher affinity for coke formation [27]. This drawback can be accomplished by the usage of promoters and supporting materials.

A broad range of inorganic metal oxides such as TiO₂, ZrO₂, Al₂O₃, SiO₂, CeO₂ and MgO have been extensively investigated as a support for nickel catalysts in reforming processes, as depicted in Table 2.1. Sutton et al. [28] examined the effect of support type on the degradation of heavy components derived from peat gasification. Even though the efficiencies of the catalysts were categorized as Ni/TiO₂>Ni/ZrO₂>Ni/Al₂O₃>Ni/SiO₂, the sample of Ni/Al₂O₃ was demonstrated as the most promising one due to its relatively lower selectivity towards methane formation. Srinakruang et al. [29] investigated the performances of three catalyst supports (alumina, silica–alumina mixed oxide and dolomite) in toluene degradation and they presented the catalytic activities in the following order Ni/Al₂O₃>Ni/SiO₂-Al₂O₃>Ni/dolomite. In spite of the lowest activity, Ni/dolomite showed stable behavior, since its basic structure promotes the formation of surface oxides, preventing carbon deposition on the catalyst surface. Miyazawa et al. [30] performed different supported nickel catalysts in steam reforming of tar mixtures obtained from wood pyrolysis process and they found the highest degradation performance for Al₂O₃ based catalyst. Kong et al. [31] conducted toluene reforming in the presence of nickel catalyst on various support materials, including alumina, silica, zirconium oxide and magnesium oxide. From the study, they found that Ni/MgO showed significant effect on the hydrocarbon cracking. This could be due to larger active area driven by smaller particle size, as well as the enhancement could be linked to higher reduction degree of nickel particles which from strong interaction with the support. In conclusion, for nickel catalysts Al₂O₃ as a support material plays an important role on thermal cracking of tar components in gasification systems because of its physiochemical stability and high mechanical resistance.

Table 2.1: Comparison of nickel catalyst with different support materials

<i>Catalyst</i>	<i>Tar Component</i>	<i>Gasification Temperature (°C)</i>	<i>% Conversion</i>	<i>Ref.</i>
Ni/SiO ₂	<i>derived from gasification of brown peat</i>	800	89.7	[28]
Ni/Al ₂ O ₃	<i>derived from gasification of brown peat</i>	800	90.3	
Ni/ZrO ₂	<i>derived from gasification of brown peat</i>	800	95.2	
Ni/TiO ₂	<i>derived from gasification of brown peat</i>	800	98.1	
Ni/dolomite	Toluene	700	92.0	[29]
Ni/Al ₂ O ₃	Toluene	700	99.0	
Ni/SiO ₂ -Al ₂ O ₃	Toluene	700	90.0	
Ni/Al ₂ O ₃	<i>derived from the pyrolysis of wood biomass.</i>	600-650	100	[30]
Ni/ZrO ₂	<i>derived from the pyrolysis of wood biomass.</i>	600-650	97.3-100	
Ni/TiO ₂	<i>derived from the pyrolysis of wood biomass.</i>	600-650	97.9-100	
Ni/CeO ₂	<i>derived from the pyrolysis of wood biomass.</i>	600-650	94.9-100	
Ni/MgO	<i>derived from the pyrolysis of wood biomass.</i>	600-650	84.3-99.2	
Ni/MgO	Toluene	600	91.2	[31]
Ni/ α -Al ₂ O ₃	Toluene	600	67.2	
Ni/ β -Al ₂ O ₃	Toluene	600	74.2	
Ni/ZrO ₂	Toluene	600	32.8	
Ni/SiO ₂	Toluene	600	11.1	
Ni/Hexaaluminate	Toluene	650	70	[32]
Ni/dolomite/La ₂ O ₃	Phenol-Toluene-Naphthalene-Pyrene	800	98.8	[33]
Ni/ α -Al ₂ O ₃	Benzene	900	90	[34]
Ni/Al ₂ O ₃	Naphthalene	800	80	[35]
Ni-Fe/Sludge	Toluene	800	90.5	[36]
Ni/Fe/Mg/Zeolite	Toluene	600	77	[37]
Ni-Co/ceramic foam	derived from coal gasification	400	90	[38]
Ni/CeO ₂ -ZrO ₂	Benzene	750	87	[39]
Ni/Al ₂ O ₃	Naphthalene	500	90-100	[40]
Ni/LaFeO ₃	Toluene	600	55	[41]
Ni/Fe ₂ O ₃ -Al ₂ O ₃	Toluene	750	80.9	[42]
Ni/Ca ₁₂ Al ₁₄ O ₃₃	Toluene	550	77.4	[43]
Ni + MnO _x /Al ₂ O ₃	Toluene	600	100	[44]

To improve catalytic activity and coke resistance, nickel supported catalysts can be promoted with different metals, as depicted in Table 2.2. Nishikawa et al. [45] examined the effect of noble metals, including Pt, Pd, Rh and Ru, on the performance of Ni/CeO₂-Al₂O₃ catalyst. Although the addition of noble metals, especially Pt, was effective in promoting steam gasification, these additives insignificantly affected coke formation. Cobalt as a promoter was also investigated and it was found that carbon deposition was limited in a considerable way [46].

Table 2.2: Comparison of promoted Ni/Al₂O₃ based catalysts

<i>Catalyst</i>	<i>Gasification Temperature (°C)</i>	<i>% Conversion</i>	<i>Coke deposition per min (wt%)</i>	<i>Reference</i>
Ni/CeO ₂ -Al ₂ O ₃	550-650	≥65	0.33	[45]
Pt-Ni/CeO ₂ -Al ₂ O ₃	550-650	≥70	>0.33	
Pd-Ni/CeO ₂ -Al ₂ O ₃	550-650	-	>0.33	
Rh-Ni/CeO ₂ -Al ₂ O ₃	550-650	≥67	>0.33	
Ru-Ni/CeO ₂ -Al ₂ O ₃	550-650	≥70	>0.33	
Co-Ni/Al ₂ O ₃	550	≥54	0.01	[46]

2.1.3.2 Secondary catalytic treatment: downstream of gasifier

Secondary catalytic treatment aims to enhance the quality of producer gas for its further utilization in power generation and production of industrial chemicals. The method is based on the catalytically conversion of tar and methane existing gasifier. It has been suggested that nickel (Ni) based catalysts are highly effective as secondary reforming catalysts for further reduction of tar as well as for adjustment of the CO/H₂ ratio through methane conversion [1, 47]. On the other hand, particulates should be removed to prevent catalyst clogging. For that, honeycomb monolith blocks deposited on catalytic material is placed directly at the gasifier outlet thereby keeping the system temperature at high level. Toledo et al. [9] suggested Ni-coated two-monolith-layer active structure for gas cleaning in a pilot-scale gasification process, as presented in Figure 2.3. Although the system showed great performance of tar reforming, the process struggled with utilization time of monoliths. To overcome this issue, the operating temperature range was determined: it should not be above 900 °C to avoid ash sticking and it should not be below 750 °C to prevent whisker type coke formation. The system is more appropriate for low-alkali content-biomass.

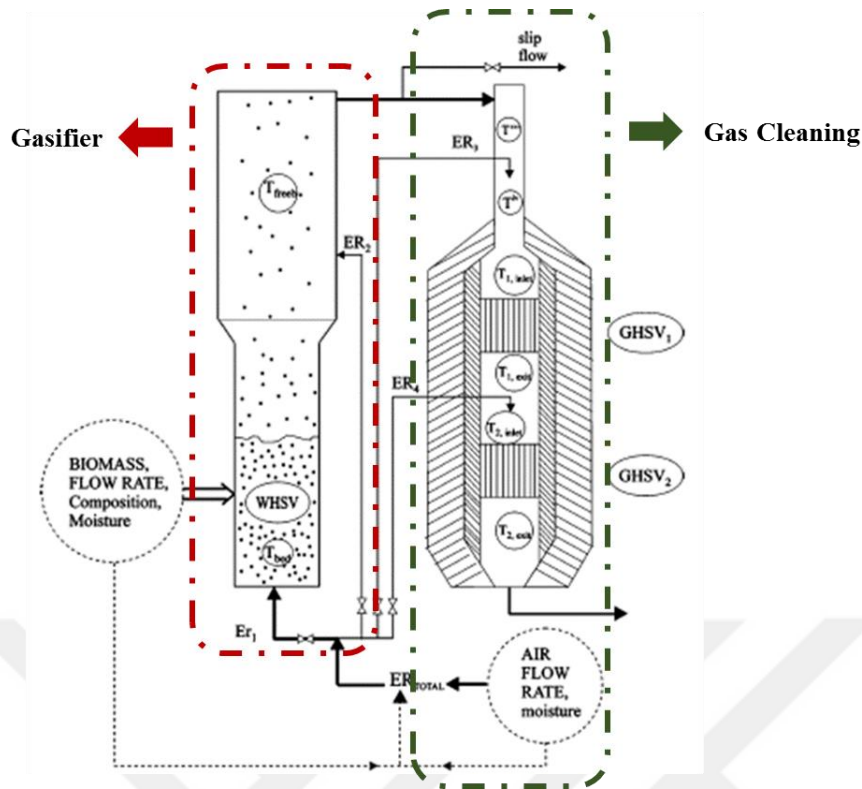


Figure 2.3: Schematic representation of gasification combined monoliths [9]

2.1.4. Unique Gasification System

"UNIQUE" gasifier system is based on the simplification and intensification of the traditional biomass gasification process by combining primary and secondary hot gas treatments in order to simultaneously remove both particulates and tar. The process integrates gasification, gas cleaning and conditioning steps into a single reactor unit in which catalytic filter elements are placed in the freeboard of gasifier as illustrates in Figure 2.4. The compact design is also cost-effective since investment cost of gas cleaning equipment are reduced as well as the space required for its installation is decreased. A further advantage is that the gas temperature is maintained stable at gasification conditions during catalytic tar reforming, thereby further step of secondary heating can be eliminated [15, 48].

In UNIQUE system, the most important part is filter medium, which has to stable at high temperatures as well as in different gas mixtures. Regarding the requirements, ceramic filters are good candidates owing to their low cost and open porous structure properties [49, 50]. The ceramic filters are divided into two groups: high-density and low-density materials. High-density filters have approximately 40% porosity, resulting

from sintered structure of silicon carbide, alumina, and cordierite, while low-density filter structures driven by aluminosilicate have up to 90% porosity. Both filter types have thermal stability in the range of up to 1000 °C and show good resistance towards gas penetration. On the other hand, the filter materials can be shaped in a candle form which is the most preferred filter geometry, resulting available integration into the freeboard gasifier [51]. Therefore, studies have focused on the development of catalytic ceramic filters via (i) filling reforming catalysts or foam inside the filter or (ii) coating into the porous structure with the catalysts.

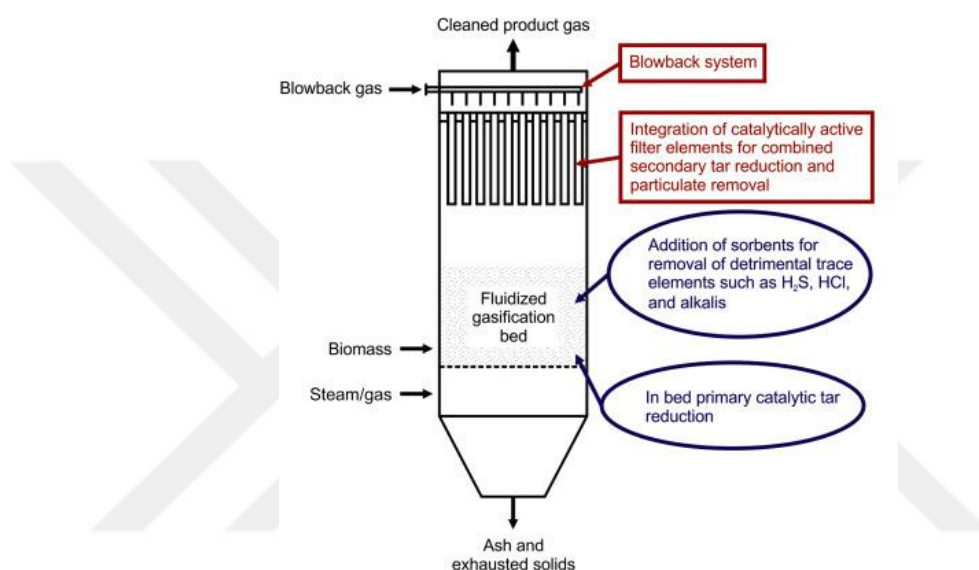


Figure 2.4: Scheme of UNIQUE gasifier concept [8]

Nickel based catalysts have been mostly considered due to their commercial availability and high selectivity for tar reforming [52-56]. The filling of Ni/MgO catalysts into silicon carbide filter was investigated by Rapagna et al. and the new catalytic filter exhibited considerable hydrocarbon conversion ratio to gas and H₂-rich product effluent, resulting improved gas yield and selectivity of water gas shift reaction. The compact system provided excellent stability during 22 h with 20 % methane and 79% tar conversions in almond-shells gasification [57]. As depicted in Figure 2.5, Al₂O₃ based ceramic filter was also filled with nickel pellets that presented a good solution for simultaneously tar and methane degradation in freeboard gasifiers. The catalytic system gave qualified synthesis gas with high heating value through hydrocarbon degradation to H₂ and CO. On the filter surface, carbon accumulation was not observed, indicating char was combusted in a considerable way.

In addition, the pressure drop was found to be acceptable region, which was attributed to sufficient gas permeation during gasification [58].

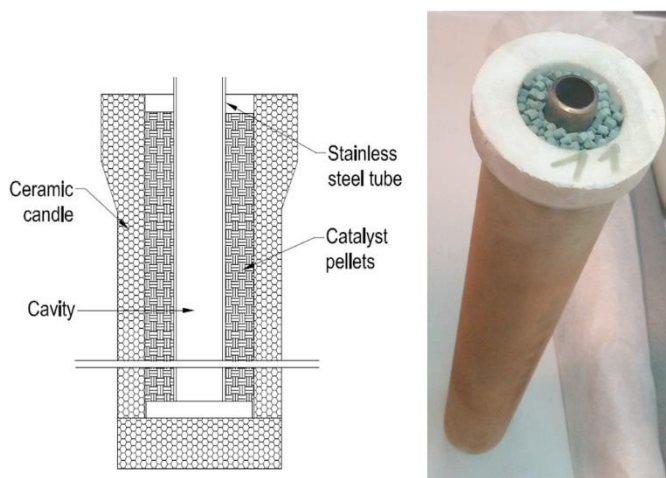


Figure 2.5: Schematic representation of catalysts filled candle filter [58]

On the other hand, nickel catalysts have been successfully coated on the porous filter structure. Zhao et al. [53] developed Ni coated alumina ceramic filter by deposition-precipitation method to utilize in naphthalene conversion. At 800 °C, the tar compound was almost converted into syngas in terms of 1 wt.% Ni loading. Engelen et al. [59] found optimum catalyst composition as 1.0 wt.% Ni + 0.5 wt.% MgO + 2.5 wt.% Al₂O₃ which was coated on filter disc. The optimum catalyst was also loaded on alumina filter material by Ma et al. [56] and they examined its activity in benzene and naphthalene reforming under gasification atmosphere, resulting markedly conversion rate. Nacken et al. [60] demonstrated efficient naphthalene conversion with Ni/MgO-Al₂O₃ coated silicon carbide filter under simulated gasification atmosphere. They depicted that the coating with MgO-Al₂O₃ increased the specific surface area of the filter material as compared to Ce, CaO-Al₂O₃, and MgO-CaO. This can be due to limited sintering behavior during calcination. Rapagna et al. [54] emphasized that Ni/MgO/Al₂O₃ impregnated silicon carbide filter, which decreased tar concentration in the producer gas, and enhanced hydrogen yield by driven by water-gas shift reaction. In a further study, this group also investigated the impregnation Ni/MgO/Al₂O₃ on filter material and observed high tar reforming efficiency in a fluidized bed gasifier in which almond shells were cracked [61]. In the catalytic structure, stable water conversion was obtained during the process of 20 h, resulting in high hydrogen concentration in the product flow. Simeone et al. [55] also exhibited

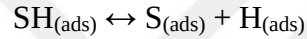
effective performance of bifunctional SiC filter, which allowed simultaneously tar and particle removal. The dual effect was achieved by sequential coating which involved a mullite membrane layer and Ni-based catalytic layer. In overall, these studies revealed that nickel coated ceramic filter can be successful utilized in advanced biomass gasification technologies. However, it was underlined that hydrogen sulfur which is generally found in the synthesis gas decreased the catalytic activity due to strong H₂S adsorption on the catalyst surface, which leads Ni poisoning and carbon deposition [54]. Thus, researchers have focused on the optimization of tar conversion in the presence of hydrogen sulfur.

The sulfur resistant property has been tried to enhance by addition of alkali metal oxides such as CaO and MgO into the nickel-based filters. Zhang et al. [62] investigated the effect of CaO amount on the Ni/ α -Al₂O₃ disc in the presence of 100 ppm H₂S and they found that the certain amount of CaO (0.5 wt.%) enhanced benzene conversion (80%) as compared to Ni/ α -Al₂O₃ (50%). Draelants [63] examined the deactivation of CaO-modified nickel-based ceramic filter disc with H₂S under gasification atmosphere containing benzene by varying temperature, sulfur concentration and velocity. It was stated that the poisoning could be limited in case of the highest temperature (950 °C) and the lowest velocity (2.5 cm/min). Furthermore, they observed that when H₂S was removed from feed gas mixture, the activity increased, indicating the deactivation was due to reversible adsorption of sulfur on Ca-sites. Another study revealed that under flow rate of 2.5 cm/min the performance of Ni/CaO based filter material on naphthalene degradation was slightly affected in a negative way [64]. On the other hand, Nacken et al. [65] examined the activities of MgO-NiO and MgO-Al₂O₃-NiO coated silicon carbide filters in the presence of H₂S and the MgO-Al₂O₃-NiO/SiC displayed higher performance on naphthalene conversion. This could be due to higher specific surface area, resulting from smaller nickel particles with better dispersion that provided less extend of sulfur deposition. Based on the research, the metal oxides incorporated Ni/Al₂O₃ ceramic filters have gained resistance to sulfur poisoning during reforming process. However, the limited tar conversion in the presence of H₂S is still an important issue in the unique gasification systems and investigations have focused on the solutions to this problem.



3.DESULFURIZATION IN BIOMASS GASIFICATION

One of the important issues for clean synthesis gas is the amount of sulfur in biomass source. During reforming process, the sulfur is mainly converted to hydrogen sulfur (H_2S), with some amounts of carbonyl sulfide (COS), carbon disulphide (CS_2), mercaptans (CH_3SH , CH_3CH_2SH) and thiophene (C_4H_4S) etc. H_2S is considered as a major constitute causes catalyst poisoning that hinders the efficiency of biomass gasification. The poisoning of nickel catalyst surface with H_2S is coincided in three ways, as observed in Figure 3.1. First mechanism, which is the most dominant, is to generate nickel sulfides via a number of steps, as follows:



In this mechanism, H_2S is immobilized by adsorption on the catalyst surface (Eq. (3.1)) and subsequently the gas molecule dissociates to its elements (Eq. (3.2)). Then, chemisorption step takes place, where chemical bond form between sulfur and nickel (Eq. (3.3)), allowing the formation of two-dimensional nickel/sulfur compound (NiS). This stage occurs rapidly and strongly, resulting from low reaction barriers [66, 67]. Another catalyst poisoning depends on the difference in chemical potential between the surface and the fluid bulk via formation of bimetallic (Ni/S) alloy which changes the geometric and electronic structure. This way causes altering reactivity, suggesting that the desired reaction can be manipulated [68]. In the third mechanism, the sulfur compounds preferentially adsorbed on undercoordinated sites which favors coke formation on the surface [69]. In other words, the sulfur negatively affects the affinity of nickel sites due to sulfide formation, alloying and carbon deposition. In addition, sulfur emissions should be considered according to stringent laws about air pollution enforcement [70]. Therefore, desulfurization is critical to maintain the activity of fuel processing catalysts, as well as it is important to avoid the corrosion of downstream equipment and to decrease the sulfur gases emissions below the regulation limits.

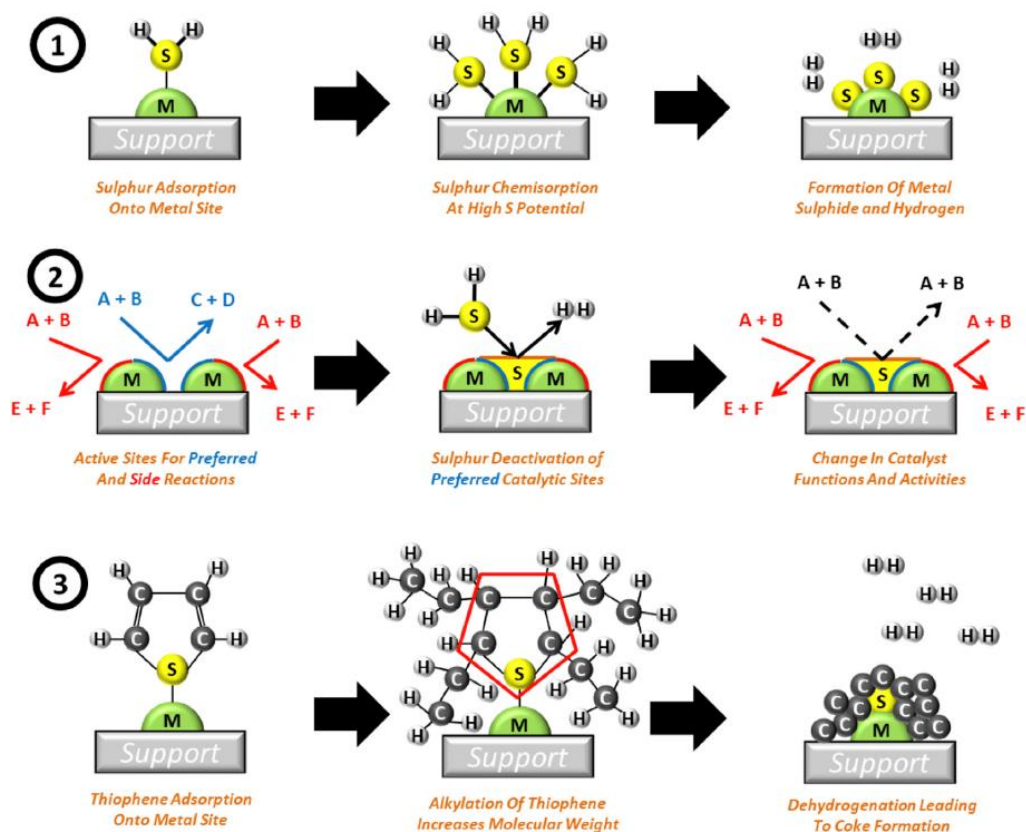


Figure 3.1: Schematic representation of Ni poisoning with sulfur [71]

In order to enable deep desulfurization in biomass gasification, three main approaches have been evolved that are feedstock treatment, development of sulfur-resistance Ni catalysts and integrated processes, as shown in Figure 3.2. In terms of feed treatment, sulfur species in biomass are removed via chemical and biological processes before thermochemical conversion. The chemical treatment can be performed by adsorption on metal oxides or hydrodesulfurization followed by adsorption. Furthermore, sulfur components can be captured by decreasing their volatility properties, which is based on bonding of sulfur species with higher molecular weight molecules [72-74]. Biodesulfurization is based on the utilization of microorganisms or enzymes as catalysts to remove organic sulfur compounds without affecting the hydrocarbon moiety [75].

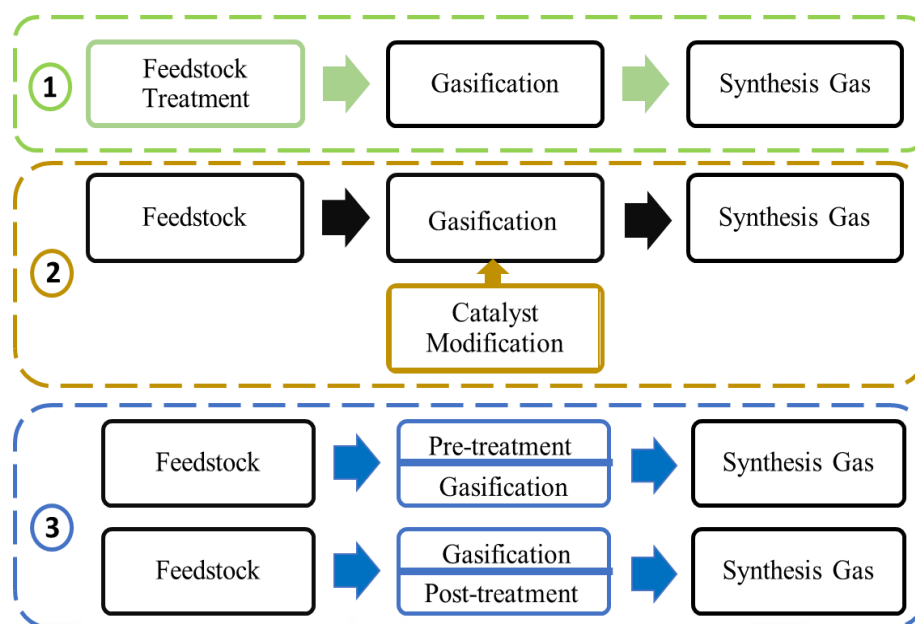


Figure 3.2: Main approaches for effective desulfurization

Another way to improve desulfurization efficiency is the modification of the nickel catalysts by incorporating of rare-earth metals, alkaline metal oxides, or noble metals which would be less prone to catalyst poisoning. Studies related to the development of the catalysts are summarized in Table 3.1. Ceria has been considered as the most common additive to inhibit sulfur adsorption on the active sites [76, 77]. Savuto et al. [78] reported that the addition ceria into nickel/magnetite catalyst structure boosted toluene degradation in the presence of sulfur, as the sulfur was selectively bonded with oxygen vacancies formed by the metal site. The improved catalyst also decreased the Ni growth, providing higher activity [78]. Furthermore, the introduction of metal oxides into the framework can enhance the sulfur resilience of the Ni based catalysts, since these materials can preferentially react with the sulfur, resulting in protecting the active sites [79, 80]. In addition, similar sulfur resistance can be obtained with noble metals (especially platinum, ruthenium, and rhodium) doped nickel catalysts [81-83]. Brady et al. [84] examined steam reforming of fuel on nickel/manganese catalyst and they reported that in the presence of sulfur the catalyst showed higher and more stable activity than non-doped nickel catalyst due to the spillover of sulfur from MnO_2 to Ni. The similar spillover behavior was also observed by Lakhapatri et al. [85] and they deduced that Rh-doped $\text{Ni}/\text{Al}_2\text{O}_3$ possessed substantially higher sulfur tolerance than $\text{Ni}/\text{Al}_2\text{O}_3$ in the steam reforming of sulfur containing hexadecane.

Table 3.1: Sulfur-resilience reforming nickel catalysts

Catalyst	Points	Ref.
CeO ₂ -doped Ni/La ₂ NiO ₄	Catalytic conversion of propane was enhanced.	[76]
CeO ₂ -doped Ni/Mayenite	The resistance to carbon deposits and sulfur poisoning were improved	[78]
Mg or B-modified Ni/Al ₂ O ₃	The addition provided slight sulfur resistance.	[79]
K-added Ni	K-promotion decreased the strength of Ni-S bond.	[80]
Rh-Ni/CeO ₂ -Al ₂ O ₃	Low temperature reforming of jet fuel was performed.	[82]
Ni-Cu, Ni-Pt, Ni-Pd on CeO ₂	Metal addition imparted sulfur resistance	[83]
NiMn	Mn acted as sacrificial element to H ₂ S adsorption.	[84]
Rh-Ni/Al ₂ O ₃	Sulfur poisoning on nickel was limited.	[85]
CeO ₂ , CaO, SrO, BaO-added Ni	Metal oxides suppressed sulfur adsorption.	[86]
La, Ba-added Ni	Stable performance was observed.	[87]
Ni on La/CeO ₂	The order of La addition affected the efficiency of autothermal reforming.	[88]
Fe-promoted NiAl	Fe inhibited nickel sintering.	[89]
Ni/perovskite	Sulfur is preferentially adsorbed on oxygen in perovskite.	[90]
Pt- Ni/Al ₂ O ₃	CH ₄ reforming was achieved at higher degree.	[91]

Integrated desulfurization methods are widely used in petroleum refineries to remove sulfur from fuel fractions. The intensified methods are generally based on scrubbing using physical or chemical sorbents. Muradov et al. [92] suggested an integrated system in which a satisfactory sulfur removal was achieved before reforming in diesel fuel production. In the desulfurization stage, a scrubber was connected with an electrolyzer that H₂S dissolved into ferric sulfate solution (Fe₂(SO₄)_{3(aq)}) via absorption. The solution was filtered to remove elemental sulfur and subsequently in the electrolyte membrane the residual solution was oxidized to obtain H₂. In this process, effective sulfur removal was observed with the enhancement of hydrogen production. On the other hand, Salehi et al. [93] developed hybrid system for sulfur removal from flue gas. As depicted in Figure 3.3a, an innovative part as adsorption/absorption (desulfurization vessel) was included in which Mg(OH)₂ impregnated ceramic foam was placed. Herein, the hydroxide solution which was continuously fed acted as a scrubbing solution. The sulfur removal performance was evaluated in the presence and absence of the Mg(OH)₂ at different temperatures

(Figure 3.3b). It was stated that the desulfurization could be enhanced with the scrubbing agent due to its higher affinity towards sulfur. The efficiency increased with temperature, providing higher energy for sulfur absorption which was consisted of higher dissolution of sulfur species into the absorbent.

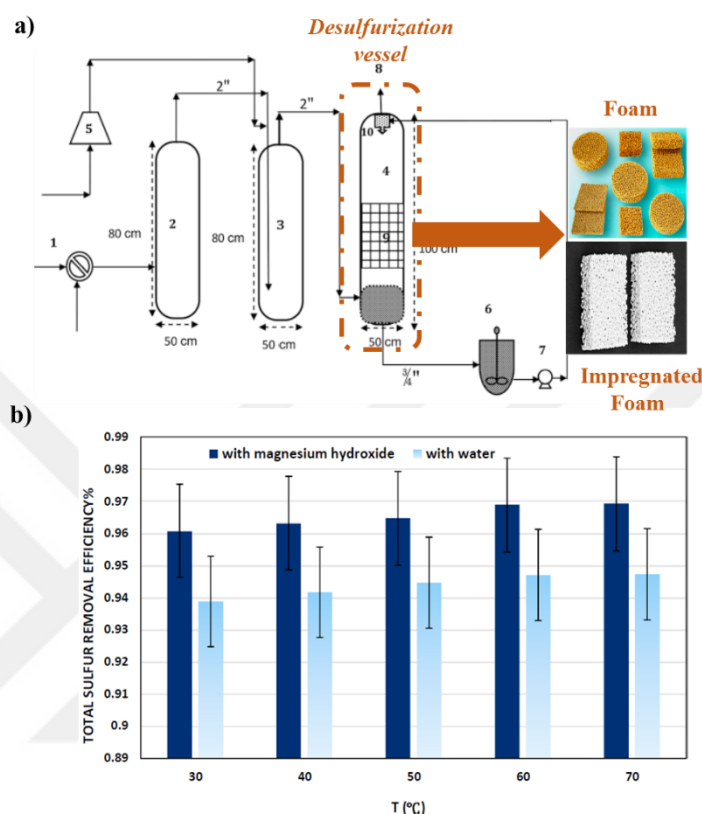


Figure 3.3: Hybrid system (a) and its efficiency on desulfurization (b) [93]

Although, the integration of reforming with scrubbing systems provided successful desulfurization, these systems could only be performed at low temperature. The biggest driving force for efficient sulfur removal in advanced technologies is the temperature range, since the removal should be carried out at high grade. In this sense, a gasification modified with hot syngas purification system was also evolved by Chan et al. [94]. The system was constructed with a fixed-bed gasifier followed by tar reformer, filter, dichlorination-desulfurization vessel, respectively. The sulfur removal process was at temperature of 400 °C was successfully performed by using Ni-Zn based adsorbents, resulting in favorable removal performance. Therefore, the integration of reforming section with adsorptive desulfurization has been generated emphatic interest for in-situ sulfur capture that is important to assess the potential of using unique gasifiers in real applications.

3.1 Adsorptive Desulfurization

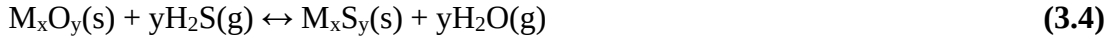
Several technologies have been successfully applied for removing sulfur pollutants to produce clean fuel. The most important ones are adsorptive, oxidative, pervaporation, extractive, hydro- and bio-desulfurization [3]. In oxidative desulfurization, sulfur compounds can be eliminated at ambient conditions in the presence of oxidant, resulting in formation of sulfone structures. However, the method is required to further step, extraction to remove the sulfones. Pervaporation desulfurization which is driven by membranes is considered as an inadequate technique owing to fouling problems. In other process, sulfur-containing species can be extracted by using a suitable solvent; however, some part of fuel can be removed during extraction. Hydrodesulfurization performs under extreme temperature and pressure conditions in the presence of catalyst, indicating a costly and difficult removal. In biodesulfurization, microorganisms or enzymes are utilized as agents for sulfur capture but it is a considerable slow process. Adsorption provides immobilization of sulfur molecules on adsorbent and no post-treatment is required to remove sulfur compounds from fuel [3, 4]. Thus, adsorptive desulfurization has been suggested as a promising technique.

Adsorption technique, which is based on dry desulfurization over solid sorbents, can be applied for desulfurization through physicochemical processes. The method efficiency is mostly dependent on the characteristics of the adsorbent which are listed. as follows:

- Sufficient activity with H_2S in a selective and fast way,
- High capacity,
- High thermal resistance and low corrosion ability,
- Stability under reductive atmosphere,
- Regenerability,
- Low cost [95].

A wide variety of adsorbent types such as metal oxide, zeolite, metal organic framework, carbon have been utilized for desulfurization. The removal efficiency is based on interaction type between the sulfur compounds and the active sites of the sorbents. The bonding can be occurred in two ways: either physical or chemical attachments [10]. Oxide materials can chemically adsorb sulfur species via acid-base interaction mechanism, which is regarded as the most selective interaction.

The presence of metal also promotes the formation of sulfur-metal interaction by transferring electron from sulfur to metal sites. The statements are attributed to high affinity for sulfur capture and the related main reaction can be generally described as follows:

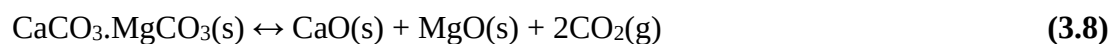
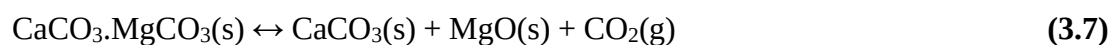


where M represents a metal. The metal-sulfides can later be converted back into metal oxide during an oxidation (regeneration) process by exposing to air or oxygen. In addition, metal oxides have a great deal of interest owing to their attractive features such as simple synthesis routes, structural stability and low cost properties [96, 97].

Iron, zinc, copper, calcium, and manganese oxides have been mainly reported as potential candidates to be utilized in hot gas desulfurization [5, 97-99]. From literature overview, it appears that iron oxides (FeO and Fe_3O_4) can be presented as the first H_2S adsorbent due to their low cost and good sulfur adsorption abilities. However, their potential is limited because of sorbent cracking problem driven by excessive reduction and iron carbide formation at a temperature higher than $550^\circ C$, as well as the reductive behavior under reduction atmosphere [100]. ZnO -based materials exhibit the most favorable sulfidation thermodynamics in the temperature range of 350 - $550^\circ C$ [5]. However, due to Zn vaporization and migration at high temperature, using ZnO as sulfur adsorbent is restricted to a temperature of above $600^\circ C$ [101]. Copper oxides (CuO and Cu_2O) can effectively reduce H_2S from several thousand ppmv to sub-ppmv levels. The adsorbents do not suffer from metal volatility problems; hence, they can be used at elevated temperature without loss of reactivity and capacity. However, in the presence of reducing components, these oxides are easily reduced to metallic Cu , which lowers the desulfurization efficiency and leads to impractical operation [102]. Calcium oxide-based adsorbents can also show an activity for desulfurization near $800^\circ C$. The most common of calcium oxides are limestone ($CaCO_3$) or dolomite ($CaCO_3 \cdot 3MgCO_3$). In terms of limestone, the thermal decomposition of the calcium carbonate followed by sulfidation occurs and the related desulfurization reactions are presented as follows:



As depicted in the reactions (Eq. (3.5 and 3.6)), the H₂S removal is restricted to calcination and the removal efficiency can only be on the order of 90% due to this limitation. On the other hand, dolomite is another alternative for Ca-based adsorbent. At higher temperatures, either (3.7) or (3.8) reaction is occurred.



That is, MgCO₃ always calcines to MgO, while the transformation of CaCO₃ to CaO depends on the CO₂ partial pressure, as well as temperature. In addition, MgO will not react with sulfur compounds, because MgS is an unstable compound under gasification conditions. According to thermodynamic equilibrium of (3.7) and (3.8) reactions, the rest of H₂S remains around 100-500 ppm, resulting unpractical application for effective desulfurization [103, 104].

Manganese oxide based materials show desulfurization activity in the moderate temperature range without any requirement for sorbent preconditioning or activation. In a reducing gas environment, MnO does not decompose to elemental manganese readily in reducing gas environment, resulting higher stability at high temperatures. However, their thermodynamics are not favorable to reach sufficient H₂S equilibrium content and they are prone to sulfate formation and have to be regenerated at very high temperature [105, 106]. Ultimately, among the other metal oxides, ZnO-based materials have received much interest in the field of desulfurization process, as the metal oxides bind strongly with sulfur compounds, yielding H₂S removal down to even fractions of 1 ppm [107]. However, this type adsorbents should be developed to utilize as an efficient desulfurizer in biomass gasification technologies by inhibiting reduction ability of elemental zinc and vaporization at gasification temperatures (700-900 °C).

3.2 Development of ZnO Adsorbents

In recent years, research efforts have been devoted to ZnO-adsorbents to improve their properties such as capture capacity, regeneration, and stability for the utilization as a hot gas adsorptive desulfurizer in biomass gasification. Studies related to the development of ZnO-based adsorbents are summarized in Table 3.2. Primarily, construction of ZnO with other metal oxides has been investigated to enhance sulfur capacity. Baird et al. [108] compared the effect of γ-Fe₂O₃, CoO, and CuO on sulfur

capture efficiency of ZnO and enhanced performance was observed in the presence of copper and cobalt oxides which created extra active sites and improved the thermal kinetics. Furthermore, NiO was utilized as a feasible additive for ZnO sorbent as it upgraded pore structure, dispersion and chemical states of active components, resulting high affinity towards sulfur compounds [109-112]. Wang et al. [113] showed that the incorporation of Ni with ZnO increased active area by higher distribution metal phases on the surface. The addition provided the formation of acid sites, leading high sulfur adsorption efficiency. It was also implied that the presence of Ni species on ZnO-Al₂O₃ increased hydroxyl concentration on the surface, indicating strong acid-base interaction [114]. Additionally, Ulah et al. [115] fabricated Ni/ZnO-Al₂O₃ as an alternative sulfur acceptor by using a free-dryer, providing ease and energy efficient synthesis way. On the other hand, it has been reported that metal oxides supported on various matrix led to remarkably enhanced desulfurization activity by affecting reaction kinetic. ZnO supported with Al₂O₃ provided their enhancement of the extend of H₂S dissociation and HS⁻ diffusion rate in ZnO bulk state, which was attributed to decreased transfer limitation [114]. Activated carbon, zeolite, and coke have also been used as support materials and they promoted surface sulfur-sorption reactions by increasing the formation of the active anion on the surface, resulting in a higher response towards sulfur compounds [116-121].

Construction of bimetallic composite structures has been presented as another approach to improve ZnO based adsorbents. Liu et al. [122] highlighted that Co-substituted into zinc lattice positively affected the adsorption reaction by synergetic effect, and the composite structure decreased vaporization ratio of Zn and the formation of sintering at high temperature. In other study, high-effective ZnMn₂O₄ based adsorbent was synthesized by Liu et al. [123] and herein, the Mn-phase improved the performance of ZnO by increasing initial desulfurization reaction. After the reaction, this phase caused rarely structural degradation during regeneration due to the fact that MnS was easily converted to MnO rather than sulfate formation. In addition, three-dimensional support remedied protection of the internal area, a result of which, the structural performance was promoted by avoiding the blockage driven by metal-sulfur compounds. The MoO₃ included Zn-based structure induced oxidation of metal-sulfur to elemental sulfur, providing sufficient regeneration [124].

Although various metal oxides could be utilized as mentioned above, iron oxide and titanium oxide (TiO_2) have been pointed out to develop Zn-based structured adsorbents. As compared to the active oxides, zinc ferrites have shown less efficiency than zinc titanates in biomass gasification, since the ferrites have shown reductive behavior under gasifier environment [125, 126]. In this sense, TiO_2 can be presented as the most interesting promotor for zinc oxide due to its special advantages: (i) higher temperature resistance against reduction, (ii) higher stability under reducing atmosphere, and (iii) decreased volatility ability [7, 127-129]. Stephanopoulos et al. [130] showed that the desulfurization efficiency of ZnO combined with TiO_2 was found to dramatically increase at higher temperatures (above 600 °C) as compared to bare ZnO. The increase was attributed to the reduced volatility and improved mechanism of ZnO. Lew et al. [101] studied the performance of zinc titanate as adsorbent for H_2S . The authors found that the formation of elemental zinc was relatively slower in case of Zn-Ti-O as compared to bare ZnO, indicating slower reduction reaction. Depending on the statements, they stated that Zn-Ti-O adsorbents are more suitable for high temperature operating conditions in the desulphurization process. In later studies, Lew et al. [131] examined the kinetics of Zn-Ti-O reduction under $\text{H}_2\text{-N}_2$ gas mixtures. They presented that Zn-Ti-O adsorbents had a lower reduction rate than pristine ZnO, resulting from the differences in activation energies of Zn-Ti-O (37 kcal/mol) and ZnO (24 kcal/mol). They also indicated that TiO_2 inhibited the sintering of ZnS by acting as a physical barrier to the growth of ZnS particles, resulting that zinc titanate materials had higher surface area and pore volume than ZnO adsorbents during desulfurization. Elseviers and Verelst [132] made thermodynamic equilibrium calculations to determine the suitable materials for deep desulfurization. Their experimental and simulation studies showed that ZnO- TiO_2 based materials are the most promising regenerable adsorbents in terms of desulfurization without any loss in activity. Ryu et al. [133] presented that Zn/Ti based adsorbent had lower specific sulfur removal in spite of its effective adsorptive efficiency. This could be due to the fact that titania did not take part in the desulfurization reaction. Polychronopoulou et al. [134] demonstrated the performance of different Zn-Ti based mixed oxides with Mn, Cu and Mo in sulfur capture under gas mixture including H_2 , CO_2 and H_2O . The additives enhanced the H_2S adsorption in recycle tests, indicating that the active phases did not decompose during the regeneration.

The kinetic behavior of zinc titanate was examined based on shrinking model, resulting that the main step during sulfurization was hydrogen sulfur diffusion through the product layer, whereas the reaction was the most important stage in regeneration [7]. In addition, the structural properties such as specific area and pore dimensions were improved by the incorporation of Al_2O_3 in Zn-Ti structure [129]. Mandic et al. [135] performed Al_2O_3 - TiO_2 - ZnO_2 as an adsorbent in hot gas desulfurization process and superior efficiency was obtained due to triple effect, which was attributed to high reactivity, chemical stability, and technical durability for ZnO, TiO_2 and Al_2O_3 , respectively. Although studies have demonstrated that the zinc titanates are promising adsorbent, their hot gas desulfurization performances does not compete with that of nanocrystalline ZnO based sorbents. In this regard, researchers have focused on the increment of sulfur adsorption capacity of Zn/Ti based materials by incorporating additives into their structures [136].

Table 3.2: ZnO based sulfur adsorbents

Catalyst	Points	Ref.
γ -Fe ₂ O ₃ , CoO, and CuO-doped ZnO	The number of sites increased in the presence of Cu or Co.	[108]
NiO/ZnO	Sufficient performance was observed.	[109]
NiO/ZnO	Long-term desulfurization was observed.	[110]
NiO/ZnO	NiO addition caused adequate regeneration.	[111]
Ni/ZnO	Ni is preferentially absorbed organosulfur compounds.	[112]
Ni/ZnO-Zn ₆ Al ₂ O ₉	Surface area and product quality were increased.	[113]
Ni/ZnO-Al ₂ O ₃	Acid-base interaction was dominant.	[114]
Ni/ZnO-Al ₂ O ₃	A facile synthesis method was proposed.	[115]
ZnO/Coke	Agglomeration was decreased during sulfur capture.	[116]
ZnO/Zeolite	Excellent desulfurization performance was attained.	[117]
ZnO-CuO/Activated carbon	Satisfactory desulfurization performance was obtained.	[118]
ZnO-MgO/Activated carbon	H ₂ S dissociation was improved.	[119]
Zn-Fe/Activated carbon	Desulfurization improved with synergistic effect of bimetallic structure.	[120]
ZnO-Co ₃ O ₄ /SiO ₂	The basicity of the adsorbent was increased.	[121]
ZnCo ₂ O ₄ / SBA-15	High stable sulfides formation and sintering were inhibited.	[122]
ZnMn ₂ O ₄ /KIT-1	The reduction of Zn was limited.	[123]
ZnMoO ₄	Regeneration was performed easily.	[124]
ZnFe ₂ O ₄	The capacity was promoted.	[125]
Zn-Fe-Ti	Carbon formation was reduced.	[126]
ZnO-TiO ₂	Reactivity was improved.	[127]
ZnO-TiO ₂	Dominant chemisorption at high temperature was achieved.	[128]
ZnO-TiO ₂ -Al ₂ O ₃	Favorable characteristics were obtained for high sulfur diffusion.	[129]

3.3 Effect of Promoters on Desulfurization Efficiency

High-efficient desulfurization have also been achieved when Zn-based adsorbents have treated with promoters, especially Co [136, 137], Ni [136], Zr [138], Cu [139] and Fe [140, 141]. Among them, copper as a promoter has gained interest due to the fact that the low melting point of copper provides to improve the properties of the host metal oxide structures during calcination, resulting in decreased agglomeration of the active phases [142]. The promoters can also enhance regeneration ability of sorbent by boosting the catalytic conversion of sulfur instead of zinc sulfate formation [143]. In addition, the additives can improve adsorption ability by forming π -complexes, which plays an important role on the desulfurization efficiency [144].

Ahmed et al. [144] observed that the addition of Cu to zinc ferrite significantly improved the desulfurization performance. The copper ions were replaced by zinc ions in the spinel structure, following the formation of mixed spinet structure which increased active phases on the adsorbents. Similar observation was observed by Mandizadeh et al. [143] in case of Cu-doped zinc ferrites as regenerable adsorbents. Mansouri et al. [145] studied with copper doped nickel-based adsorbent and they concluded that the incorporation of copper into the structure changed the electronic properties. The enhanced electron mobility improved the reducibility of NiO that was attributed to more active sites. Guo et al. [146] stated that the addition of copper enhanced sulfur adsorption ability of mesoporous carbon-SiO₂-Al₂O₃ nanocomposites by increasing the acidity that contributed to higher extent of adsorption driven by π -interconnection. Falco et al. [118] demonstrated that Cu-promoted Zn-based adsorbent involved an improved desulfurization capacity due to enhanced diffusion through the ZnS layer, indicating outward growth of ZnS was limited. Elyassi et al. [98] revealed that Cu substitution into the host lattice prevented clogging of porosity during desulfurization, resulting higher degree of ZnO utilization. This phenomenon was confirmed with the SEM images of the as-obtained sorbent before and after the reaction (Figure 3.4).

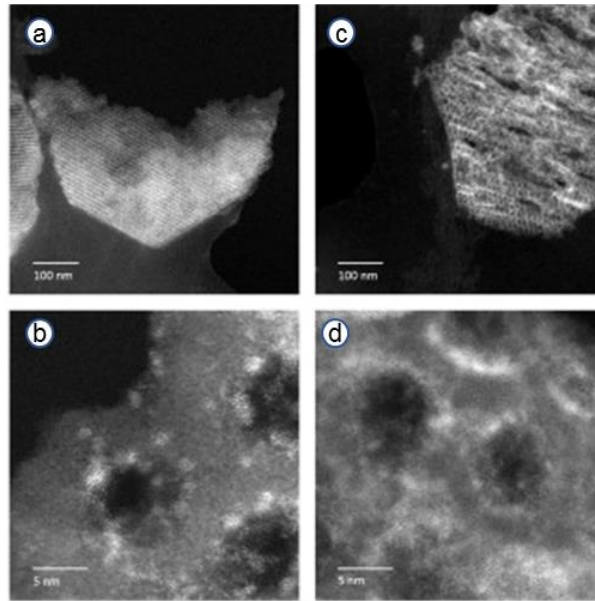


Figure 3.4: SEM images of fresh (a,b) and spent (c,d) Cu-ZT adsorbents [98]

Lie et al. [147] prepared structured Cu-ZnO-Al₂O₃ adsorbent via condensation and calcination steps, as seen in Figure 3.5a. The presence of Cu in first stage improved the reactivity, since H₂S primarily decomposed on it, then the sulfur was attached on ZnO, resulting higher degree of Zn-S interaction. Thus, the adsorbents exhibited high performance with regard to ZnO amounts (Figure 3.5b).

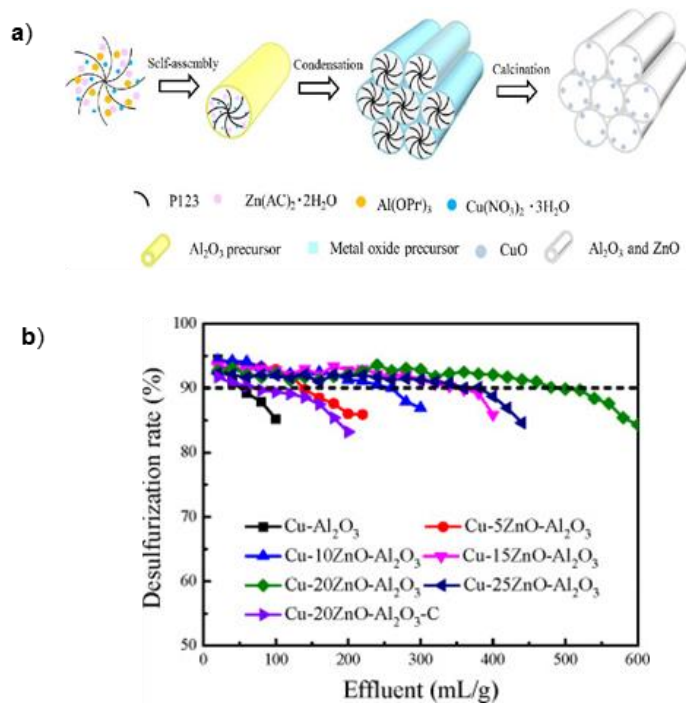


Figure 3.5: Synthesis method (a) and performances (b) of Cu-ZnO-Al₂O₃ [147]

In addition, Yuwapornpanit et al. [148] demonstrated sulfur capture pathway on copper-doped active materials (Figure 3.6). The adsorption could take place in four stages: (1) physically sorption of sulfur compounds, (2) hydrogenation followed by sulfur leaving hydrocarbon, (3) simultaneously desorption of the rest carbon-rich structure and the chemically bonding Cu and S. It was also postulated that the highest Cu-S bond might be formed after migration of hydrocarbon product from the surface.

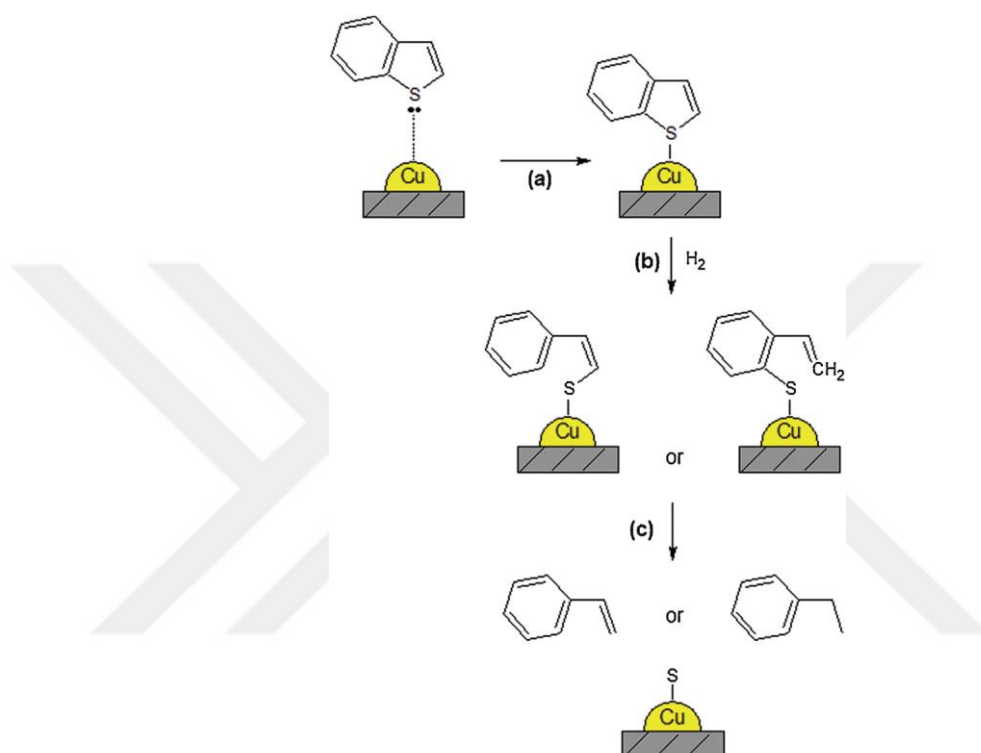


Figure 3.6: Schematic representation of sulfur compounds adsorption on Cu sites [148]

3.4 Adsorption Mechanism of ZnO-Based Adsorbents

A beneficial approach to determine the extent of adsorption should start with defining reaction domains, which are generally assigned to thermodynamics and mass transfer mechanisms. In the heterogenous system, the main reaction is controlled as follows:

- (i) Diffusion of the adsorbate from the bulk fluid to the external surface of the adsorbent pellet,
- (ii) Diffusion of the adsorbates through the adsorbent pores,
- (iii) Adsorption of the adsorbates onto the surface inside pores,
- (iv) Reaction on the surface.

It can be stated that the sulfidation process at high temperatures is mainly governed by two stages: micropore and macropore diffusions, which are attributed to external and internal mass transfers, respectively [149, 150]. The kinetic study which describes the influences of different resistances on the conversion-time profiles poses great importance in developing oxide adsorbents for hot coal gas desulfurization.

In past decades, kinetic studies have been performed by applying shrinking core and grain model for the gas-solid reaction [151-154]. According to the shrinking core model, the reaction occurs at interface between the active surface and the interior core of the adsorbent pellets. During the sulfidation, the unreacted core gradually shrinks while the product layer increases until the whole solid pellet is completely reacted. This model can be only used for micro-size particles, as the rate-limiting step is the chemical reaction. On the other hand, solid particles are generally formed by the accumulation of grains, thereby the sulfidation can be explained by considering both micro and macro parameters [151, 152]. This can be done by applying the grain model. Based on this model, the grain size increases during sulfidation, resulting in decreased pore size, thereby the transfer path of sulfur compounds inside the adsorbent is blocked. The blockage can be minimized in case of small particle size. In addition, each grain is considered as a shrinking nonporous core and the core is reacted with hydrogen sulfide, resulting the formation of nonporous sulfide product layer [153, 154].

During the sulfidation, the external mass transfer can be explained by the following steps as illustrated in Figure 3.7a:

In step 1: H₂S is adsorbed followed by dissociation on the surface (Eq. (3.9)).



In step 2: ZnS is formed by the reaction between HS⁻ and ZnO (Eq. (3.10)).



In step 3: H₂O is desorbed (Eq. 3.11), which is produced by the bonding of the rest active sites (OH⁻ and H⁺).



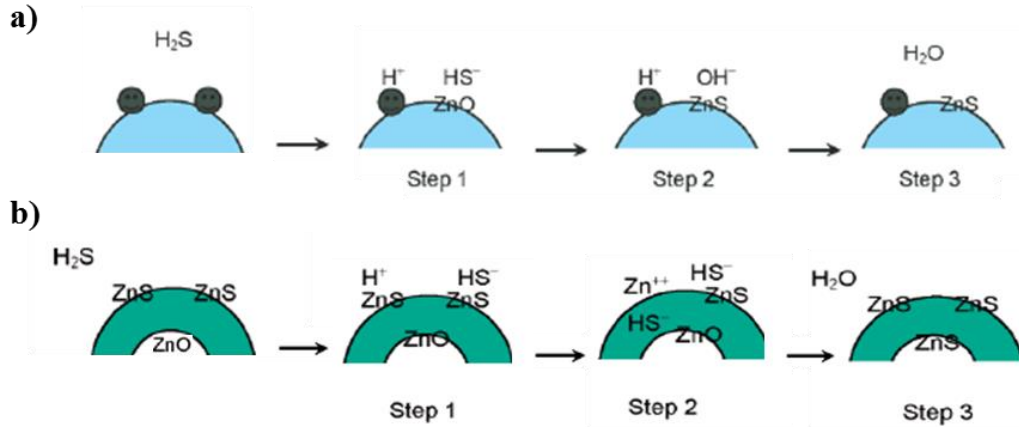


Figure 3.7: External (a) and internal (b) diffusion ways during sulfurization [155]

The external transfer mechanism is prevailing until the total grain surface of ZnO is transformed into ZnS . For further sulfidation, H_2S diffuses through the product layer (ZnS), then it reacts with ZnO underneath. This diffusion step is slower than the initial surface reaction, indicating that the penetration transfer is important for the degree of the sulfidation. In case of the sulfur adsorption reaction, the transfer type can be assigned to internal mass transfer mechanism and it can be described by the following steps as seen in Figure 3.7b:

In step 1: the sulfur molecule is absorbed on the ZnS crystal and the two active sites are occurred .

In step 2: HS^- is moved through the ZnS structure and it is reacted with ZnO underneath (Eq. (3.13)). Subsequently, outward ion migration of OH^- , which produces during the ZnS formation, is occurred.

In step 3: the OH^- diffused out and the H^+ formed are reacted each other to form water molecule, resulting water desorption from the surface.

According to the stages, the adsorbent capacity is progressively consumed due to the difficulty of the H_2S molecules to reach the fresh particles inside the material [155, 156]. The reaction model should be regarded with the influence of external mass transfer, pore diffusion, and product layer diffusion resistances. With the proper choice of particle size, flow rate and operating temperature, the product layer can be considered to be the only resistance to be dealt with [149, 150].



4. MATERIAL AND METHOD

4.1 Materials

All chemicals used in this study were of analytical grade and were used directly without purification. All aqueous solutions were prepared using de-ionized water. Zn_2TiO_4 powder (200 mesh) with 99.9% purity on metal basis was supplied from Alfa Aesar. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), titanium(IV)isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) and copper(II) chloride (CuCl_2) were supplied from Sigma-Aldrich. Ammonium hydroxide (NH_4OH) was purchased from VWR BDH Prolabo Chemicals, and hydrogen peroxide (H_2O_2), nitric acid (HNO_3), ethanol and isopropanol were procured from GR Merck in zinc-based samples synthetization stage.

Tenmat CS1150F filter material with 480 kg/m^3 density was purchased from Tenmat Ltd. (UK). The filter was cut as discs, which had approximately 25 mm diameter and 10 mm thickness. In addition, nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and dispersible boehmite powder (Disperal HP14, Sasol Italy SpA) were supplied to coat the filter samples. The boehmite powder had considerably high surface area ($>150 \text{ m}^2/\text{g}$).

4.2 Synthesis Procedures

4.2.1 Synthesis of Cu-Doped Zinc Titanates (Cu-ZT)

An oxalate co-precipitation method has been considered as a promising way to prepare titanate based powders, as the chemical technique is performed with high reactive precursors that provides several advantages such as high degree of crystallinity, narrow particle size distribution, short synthesis time and low calcination temperature [157, 158]. Thus, herein zinc titanates were synthesized by oxalate co-precipitation method through following steps mentioned in a previous study [159]. At first, titanium hydroxide ($\text{Ti}(\text{OH})_4$) was precipitated with the reaction of $\text{TiO}(\text{C}_3\text{H}_7)_4$ and NH_4OH in aqueous environment, and subsequently the solid phase was dissolved in an acidic media including HNO_3 (6 M) and H_2O_2 (30%). Then, a certain amount of zinc nitrate solution was added into the as-obtained solution under rigorous stirring at 30°C in order to achieve rapid co-precipitation. The molar ratio of $[\text{Zn}^{2+}]/[\text{Ti}^{4+}]$ was 2.0 for the starting synthesis batch. The obtained gel was then thoroughly mixed for 10 min until

a homogeneous suspension was formed, and then the final pH of the solution was adjusted to 5. The precipitate was filtered, subsequently washed with distilled water up to the complete neutralization and dried under air atmosphere at 90 °C for overnight. The final product was obtained, after calcination at 800 °C for 3 h. The sample was coded as ZT. In case of copper doped zinc titanates, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were added together with the aqueous $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution in the amounts corresponding to 2 wt.%, 4 wt.% and 6 wt.% copper based on the theoretical synthesis. In further stage, the steps in ZT synthesis were applied in a similar way. The samples were named as 2%Cu-ZT, 4%Cu-ZT and 6%Cu-ZT. The synthesis methods were schematically presented in Figure 4.1.

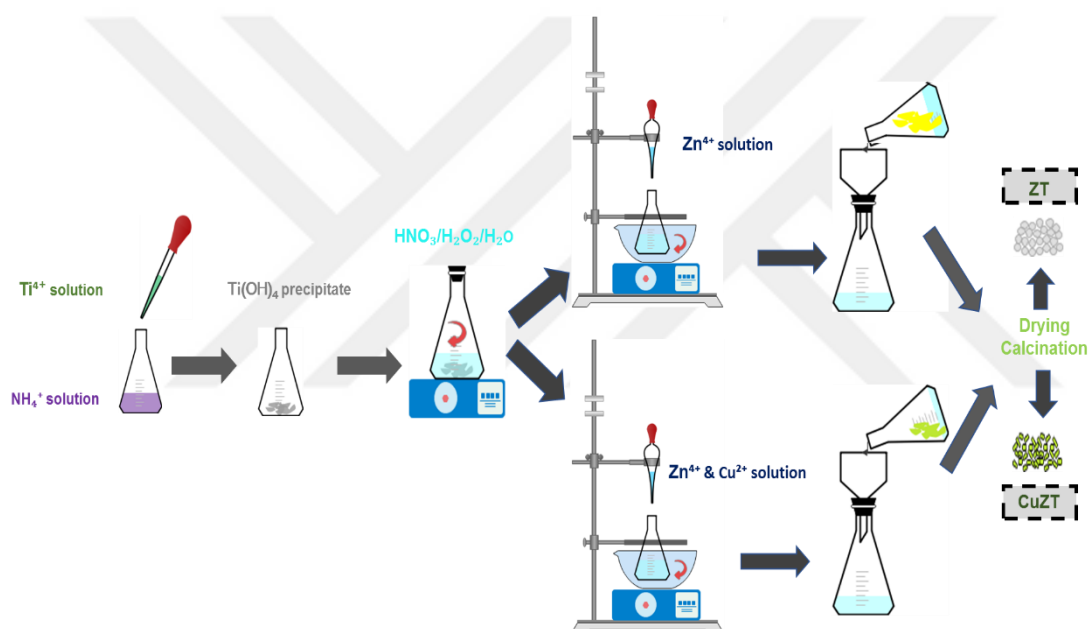


Figure 4.1: Schematic synthesis of ZT and Cu-ZT samples

4.2.2 Synthesis of Cu-ZT Incorporated with Ceramic Filters (CuZT/p-CF)

The incorporation of Cu doped ZT sample with calcium silicate based ceramic filter was carried out by wet ball-milling process which allows sufficient surface coating for particles in small size. For the method, the main principle is considered as: the host material surface is activated by collision driven the movement of balls and then the ball-induced surface species are strongly bonded with the coating materials [160].

In this part, 6%Cu-ZT (coded as CuZT) was applied for the incorporation with ceramic filter. Before ball-milling process, the filter sample was firstly grounded with a mortar

and the powder substance (p-CF) was later calcined at 900 °C to increase and stabilize surface area [161]. The different weight percentages of CuZT were mixed with a certain amount of the p-CF. The powder mixture in 10 mL ethanol was put into the agate jar and the same amount with the total sample of agate balls (stainless steel) was added into the jar. The agate jar was placed in a ball-mill machine. Then, it operated 300 rpm for 5 min, and subsequently 500 rpm for 5 min. The resultant powder was washed with ethanol and dried at 90 °C overnight. Subsequently, the powder was calcined at 450 °C. The as-obtained samples were labelled as 5%CuZT/p-CF, 10%CuZT/p-CF, 15%CuZT/p-CF and 20%CuZT/p-CF, according to the theoretical percentage amount of CuZT. The method was depicted in Figure 4.2.

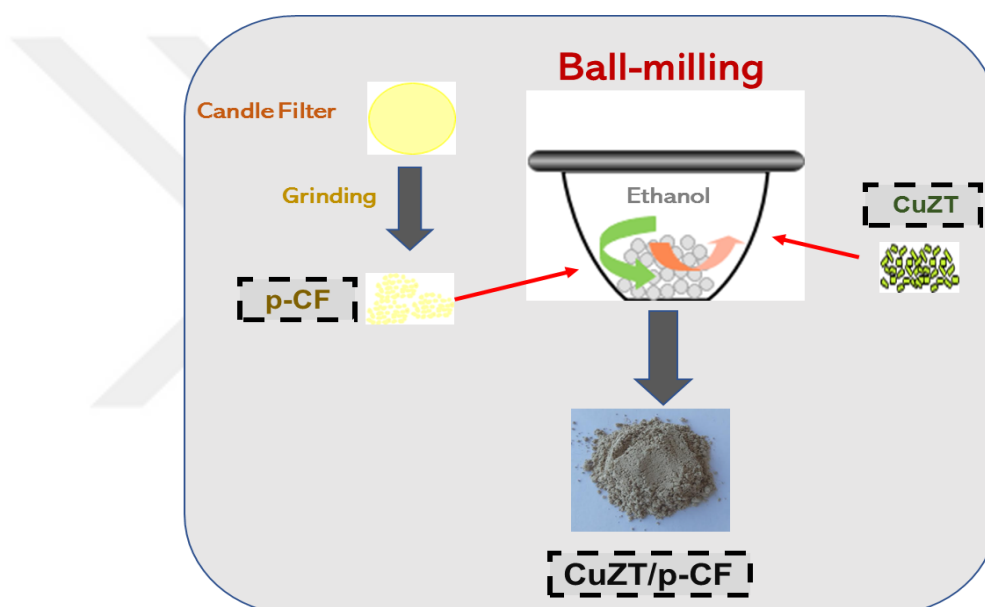


Figure 4.2: Schematic synthesis of CuZT/p-CF samples

4.2.3 Synthesis of Ni/Al₂O₃ Coated Ceramic Filter (Ni/Al₂O₃/d-CF)

The calcium silicate-based filter was activated by coating with Ni/Al₂O₃ to be utilized in steam methane and benzene reforming, as presented in Figure 4.3. Primarily, the blank disc was calcined at 900 °C for 4 hours and a colloidal solution was prepared by using boehmite powder in acidic environment including de-ionized water and HNO₃ (pH=3-4). Then, the as-calcined disc was coated with boehmite solution by applying colloidal impregnation which gives opportunity to well interaction between the filter and the alumina-based sol [162]. Herein, the solid/ liquid ratio was determined as 1.75. The as-coated disc was calcined at 600 °C, which would increase the specific surface area of the filter sample for efficient nickel loading. In other step, NiO phase was

attached on the Al_2O_3 -coated disc by performing dry impregnation of the nickel salt solution (including 50% nickel salt). After drying at 90°C for overnight, Ni-coated disc was calcined at 450°C . The sample was coded as Ni/ Al_2O_3 /d-CF.

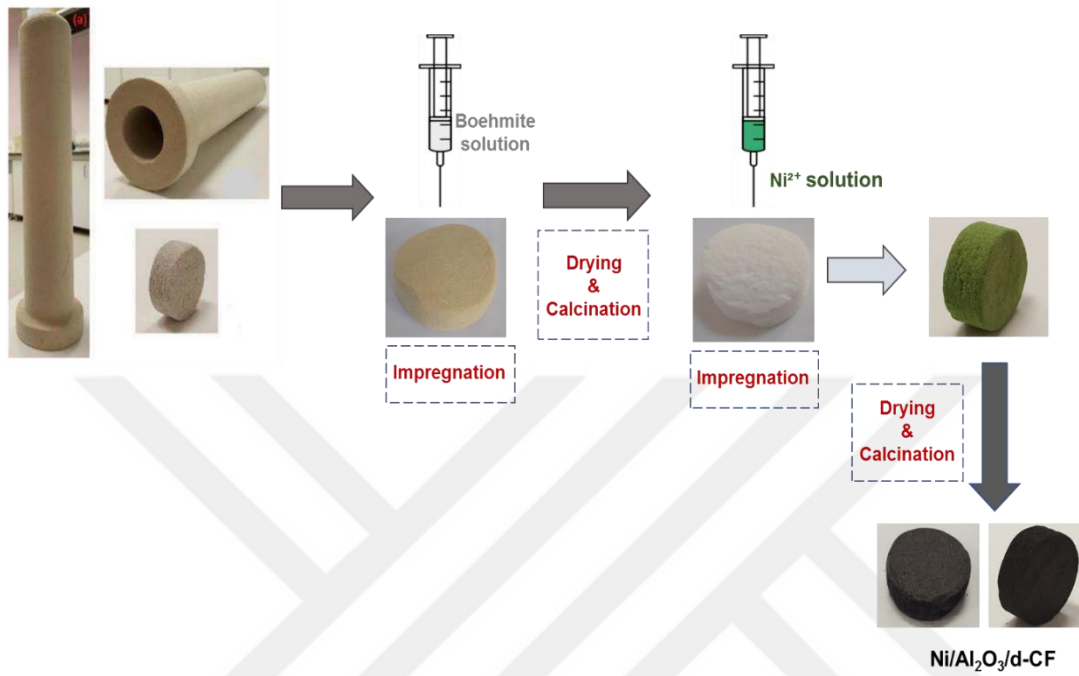


Figure 4.3: Schematic synthesis of Ni/ Al_2O_3 /d-CF sample

4.3 Characterization

4.3.1 Brunauer-Emmett-Teller Analysis

Brunauer-Emmett-Teller (BET) surface area measurements were carried out at -196°C on a HIDEN IGA03 gas sorption system. The analyses were performed for the bare (ZT) and copper-doped zinc titanate adsorbents (2,4,6%Cu-ZT) to examine the effect of copper amount on the surface area. Primarily, approximately 0.02 g adsorbent was placed into a glass tube and purged in a flow of N_2 overnight at 383K. Then, the related measurement was performed. The result values were determined using the adsorption branch of the N_2 -isotherm, which can be considered as an extension of Langmuir theory [163]. The BET equation can be expressed as follows:

$$\frac{1}{v[(\frac{P_0}{P})-1]} = \frac{c-1}{v_m c} \left(\frac{P}{P_0} \right) + \frac{1}{v_m c} \quad (4.1)$$

where P and P_0 are the equilibrium and the saturation pressure of nitrogen molecules at specific temperature, also v and v_m are the adsorbed and monolayer adsorbed gas quantity (in volume units), as well as c is the BET constant considered by Eq. (4.2),

$$c = \exp \frac{E_1 - E_C}{RT} \quad (4.2)$$

where E_1 is the heat of adsorption for the first layer, and E_C is the heat of condensation, which is attributed to the energy for further layers. The isotherm is obtained as a straight line with $1/v[(P/P_0)-1]$ on the y-axis and P/P_0 on the x-axis. According to the y-intercept values of the line, the monolayer adsorbed gas quantity (v_m) is calculated and by using the value total surface area (S_{total}) and specific surface area (S_{BET}) can be determined by the following equations;

$$S_{total} = \frac{v_m N s}{V} \quad (4.3)$$

$$S_{BET} = \frac{S_{total}}{a} \quad (4.4)$$

where N is the Avogadro's number, s is the adsorption cross-section (for N_2 , $s = 0.16 \text{ nm}^2$), V is molar volume of adsorbed gas (22.4 L/mol), and a is molar weight of adsorbed species [163].

4.3.2 X-ray Powder Diffraction

X-ray diffraction (XRD) measurements were implemented in order to identify crystal phases of all as-prepared active materials. For this method, the materials were slightly grounded by using agate mortar and the fine powders were attached on Si angle crystal sample holders with the adhesion strength provided by alcohol-based solution. Then, the peak profiles were obtained by a PANalytical PW3040/60 X-ray diffractometer using $\text{Cu(K}\alpha\text{)}$ radiation source in the 2θ range of 20° – 80° with a sampling step of 0.02 . In further analysis, diffraction data from International Centre and database PDF from HighScore Plus (PANalytical, 2004) were used to determine the lattice structures and phases. In addition, the characterization method was applied for selected as-used samples to observe the sulfur adsorption effect on the crystal phases.

4.3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron (XPS) measurements were performed using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. Principally, the sample was pressed into a

pellet which was exposed by single-energy X-ray photon irradiation under high vacuum. Then, the irradiated-photoelectrons on the adsorbent pellet were emitted and finally the electrons were counted over a range of electron kinetic energies to obtain the related spectrum. In this study, the surface electronic states of ZT and 6%Cu-ZT adsorbents were determined to examine the incorporation of copper-states in the zinc titanate lattice. In addition, the role of Cu as a promoter in desulfurization was investigated via observation of Cu2p_{3/2} state and oxygen peaks with high-intensity in terms of 6%Cu-ZT sample.

4.3.4 Fourier-Transfer Infrared Spectroscopy

Fourier-transfer infrared (FTIR) measurements were obtained by a Perkin Elmer Spectrum 100 Fourier transform infrared spectrometer to monitor the change in filter surface chemistry with the addition of copper-doped zinc titanate into the lattice. The spectral data of the samples were collected between 1500-600 cm⁻¹ with attenuated total reflectance method (ATR) which is attributed to the most common FTIR technique owing to short process time and non-required pretreatment. This method was performed by using a crystal with a high refractive index and excellent IR transmitting properties.

4.3.5 Scanning Electron Microscopy/Energy-Dispersive X-ray Spectroscopy

Scanning electron microscopy technique was conducted to observe the samples by scanning with a high-energy beam of electrons. Before imagination, gold sputter-coated was applied to powder samples. At 20,000x magnification, the high-resolution imaging method was performed to observe the surface topography of the fresh materials (ZT and 6%Cu-ZT samples). Furthermore, the incorporated filter with Cu-ZT (20%CuZT/p-CF) and spent adsorbent were imaged. Point specific elemental analysis by the EDX detector attached to the SEM instrument was also utilized to estimate the amount of sulfur atoms attached on the surface, and to determine the amount of the constituent ions (Zn, Ti, O and Cu ions). Additionally, elemental mapping was performed to observe the spatial distribution of elements (carbon and nickel) on nickel-activated filters (Ni/Al₂O₃/d-CF). The related analyses were performed using Bruker SEM-EDAX and Carl Zeiss 300VP SEM-EDX devices.

4.3.6 Transmission Electron Microscopy

Transmission electron microscopy (TEM) in which a beam of electrons is transmitted through a specimen to obtain an image was applied to characterize the structure of grains using a JEOL 2100 JEM HRTEM electron microscope. After the samples were coated with gold, the images were recorded with an enhanced resolution (1 μm & 500 nm) to evaluate dependency of product layer formation on temperature.

4.4 Experimental Set-up

4.4.1 Adsorptive H₂S Removal

H₂S removal studies were conducted in a laboratory-scale fixed bed reactor, as depicted in Figure 4.4. Adsorbent materials were placed in a vertical 310 grade stainless-steel tubular reactor with the length of 1085 mm and inner diameter of 14.7 mm. To ensure temperature uniformity during the experiments, a three-split furnace was used to achieve process temperature maintained by using a PID temperature set point controller. Gas components stored in individual cylinders were fed into the reactor, after the required gas components were mixed in a chamber. Steam was generated with an electrically heated evaporator and it was transferred to the reactor with nitrogen gas. All lines in the system were heated to prevent condensation. Prior to the gas analysis, the effluent gas mixture was passed through a water trap. In addition, the reactor system had a bypass flow line for feed analysis. The analyses were performed using two different instruments and the detailed information was presented in the following sub-sections (4.4.4.).

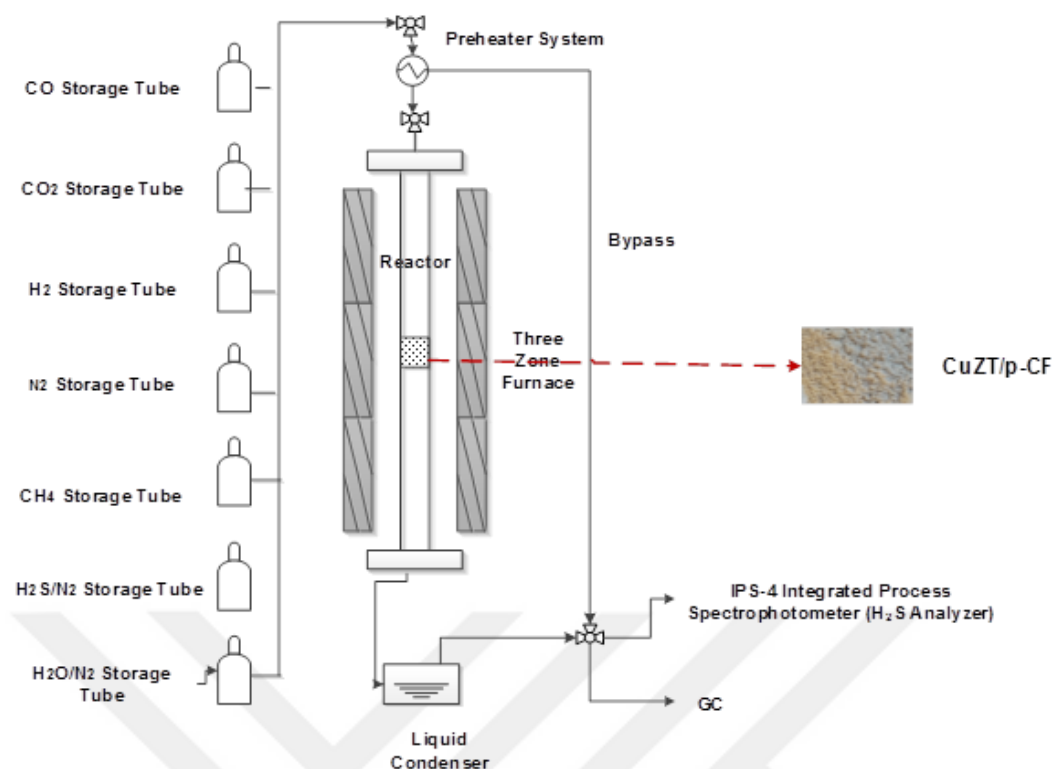


Figure 4.4: Schematic diagram of H₂S adsorption

The desulfurization studies were conducted in the presence of 200 ppmv H₂S and for the experiment details were summarized in Table 4.1. For commercial zinc titanate (ZTC), preliminary experiments related to fluid rate were performed under a constant residence time (1 g adsorbent/ H₂S-N₂ L/min gas flow) in inert atmosphere. The second performance test groups were carried out by applying various temperatures under the inert flow. In third part, the activity was evaluated under reducing, oxidizing and dry gasification environments. Furthermore, the adsorption efficiencies of the as-synthesized Cu-ZT adsorbents were monitored in inert, reducing and dry gasification atmospheres. In addition, CuZT incorporated- CaSiO₃ filters were performed in the desulfurization process under inert and reducing atmospheres, as well as gasification environment including methane and steam. All experiments were performed three times and the range of the results which includes the highest and lowest values of the activities were showed in the performances curves. In addition, the image of the system was presented in Figure 4.5.

Table 4.1: Conditions for desulfurization experiments

Adsorbent	Desulfurization Conditions			
	Tem. (°C)	Flow Rate (L/min)	Amount (g)	Reaction Atmosphere
ZT _C	750	1	1	N ₂
	750	2	2	N ₂
	750	3	3	N ₂
	450	2	2	N ₂
	600	2	2	N ₂
	750	2	2	N ₂
	750	2	2	20%H ₂ / N ₂
	750	2	2	1%H ₂ O/N ₂
	750	2	2	15%CO/17%CO ₂ /20% H ₂ /1% H ₂ O/N ₂
Cu-ZT	750	2	2	N ₂
	750	2	2	20%H ₂ / N ₂
	750	2	2	15%CO/17%CO ₂ /20% H ₂ /N ₂
Cu-ZT/p-CF	750	2	2	N ₂
	750	2	2	20%H ₂ / N ₂
	750	2	2	15%CO/17%CO ₂ /20%H ₂ /5%CH ₄ /1% H ₂ O/N ₂

4.4.2 Steam Reforming

The reforming activities of Ni/Al₂O₃/d-CF were evaluated by using similar set-up with desulfurization apart from the reactor (Figure 4.4 & 4.5). For the disc-based sample, a stainless-steel tubular reactor with the length of 1085 mm and the inner diameter of 26 mm was used. Primarily, the catalyst was reduced under 10%H₂/90%N₂ flow at 500 °C overnight. Then, the hydrogen flux was interrupted, and the temperature was increased to 750 °C under nitrogen flow. After the temperature value was stabilized throughout the reactor, the methane reforming was performed under the simulated steam-included synthesis gas flow (2L/min) with H₂S and without H₂S mentioned in the previous section. The reaction was also carried out by adding 2 g/h benzene in the inlet-flow to observe simultaneously benzene and methane degradation over the as-coated disc in the presence of hydrogen sulfur. The outlet gas effluent was specified by using the methods mentioned in subsection 4.4.4. In addition, the residual benzene was trapped into isopropanol and then, the amount of benzene was determined with a gas chromatography detailed below. The experiments were performed three replicates and the range of the results were shown in the performances curves.



Figure 4.5: Experimental set-up for H₂S adsorption

4.4.3 Integrated Reforming and Desulfurization Process

To achieve H₂S and methane/benzene removal at the same time, a lab-scale system including of two reactors connected in series with each other was settled, as presented in Figure 4.6. The first tubular reactor was utilized in the desulfurization process while the disc samples was placed inside the second reactor. The specifications of the reactors were mentioned in the previous sections. In this section, 20%CuZT/p-CF and Ni/Al₂O₃/d-CF filters were utilized for H₂S adsorption and reforming reactions, respectively. After the filter materials were placed in the relevant reactors, the tubular bodies were placed in one split-type furnace. Simulated gas mixture was formed by using mass flow controllers and steam was sent into the reactor system, after the evaporation of required water with an electrically heater. Before the reaction, the active sample was reduced at 500 °C under flow (10% H₂, 90%N₂). The catalytic activity tests were performed under both the simulated H₂S-free synthesis gas environment and the H₂S-included gasification atmosphere at 750 °C. The reaction set was also conducted in the presence of benzene (2 g/h). The benzene amount was adjusted as

equivalent to 15 g C/Nm³. The specification of gas and liquid products were carried out by applying the methods explained in 4.4.4. section.

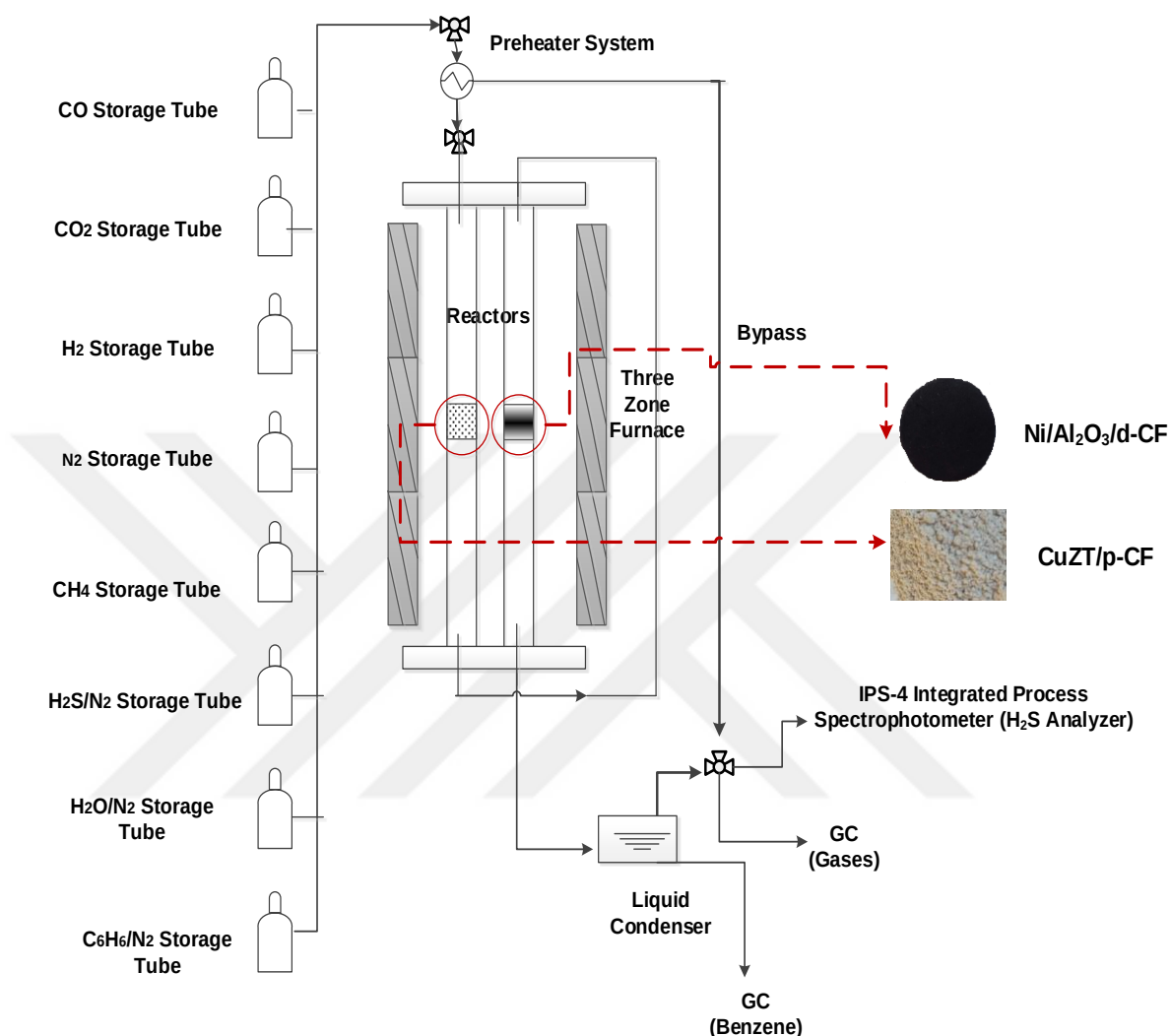


Figure 4.6: Experimental set-up for integrated process

4.4.4 Effluent Analysis

4.4.4.1 H₂S analysis

Herein, the amount of H₂S in outlet streams were determined using Model IPS-4 Integrated UV-VIS Process Spectrophotometer by AMETEK, Inc. As depicted in Figure 4.7, the online specification method is related to an array-based optical system, in which the flow is send to a sampling cell and its optical properties are examined. In this study, the cell including sample probe was operated at 85 °C and UV spectra was recorded between 200-250 nm with regard to the absorbance wavelength of H₂S

(225 nm). Furthermore, the related values were recorded for each 10 minutes by using data processing software. Before experimental study, the reliability of the method was checked by measuring gas streams containing different concentrations of H₂S (1-200 ppm) and then, the quantity of H₂S in feed streams were analyzed with the spectrophotometer by using bypass line of the reactor system.

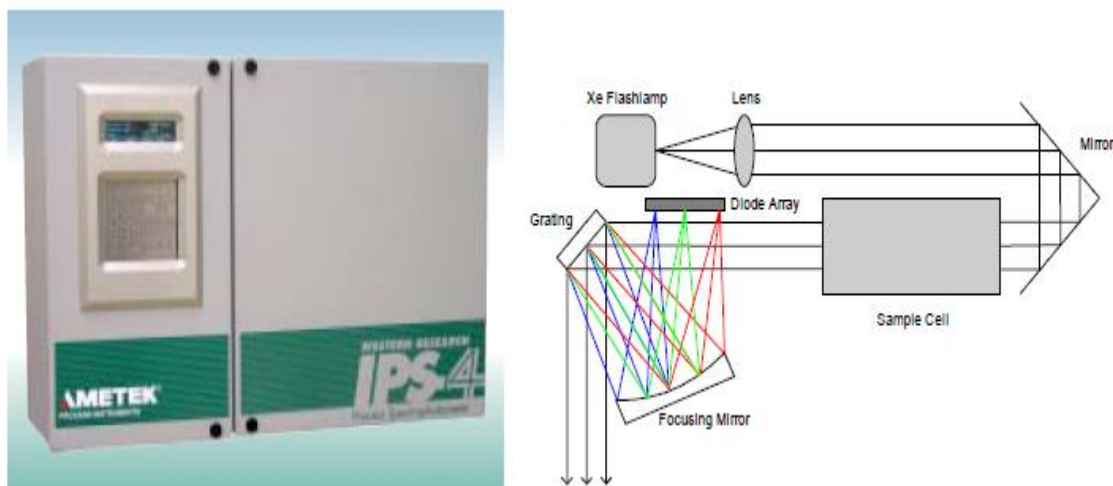


Figure 4.7: Schematic presentation of H₂S optical analysis system [164]

The sulfur capture efficiency was considered as hydrogen sulfur conversion which was calculated with the equation below:

$$X_i \% = \frac{H_2S_{in} - H_2S_{out}}{H_2S_{out}} \times 100 \quad (4.5)$$

where X_i is the conversion of the H₂S; H_2S_{in} and H_2S_{out} are the inlet and outlet the amounts of the component.

4.4.4.2 Permanent gas analysis

The identification of components in gas flow produced from test-rig was conducted by a gas chromatography (Agilent 7890A) equipped with one flame ionization detector (FID) and two thermal conductivity detectors (TCD). The TCD channel with packed columns was used to measure H₂, CO₂, N₂, CH₄ and CO. The oven temperature was programmed to increase from 45 to 120 °C. The column temperature was set at 250 °C. All injections were performed in a splitless mode and the detection time was determined as 10 min.

The device was calibrated by analyzing with calibration tubes with known gas concentrations (5% CH₄, 5% CO, 20% CO₂, 30% H₂ and 40% N₂) and the accuracy of the method was controlled with the tubes before each experiment. In addition, the quantities of gas components were determined as volumetric percent value in flow with regard to their peak areas in chromatograms and the methane conversion was calculated by using the equation below:

$$\text{CH}_4 \text{ Conversion \%} = \frac{V_{\text{in}} - V_{\text{out}}}{V_{\text{out}}} \times 100 \quad (4.6)$$

where V_{in} and V_{out} are the volumetric percentage amount of the methane in inlet and outlet streams, respectively.

4.4.4.3 Benzene analysis

In this study, benzene analysis was performed using GC which includes flame ionization detector. The trapped benzene in isopropanol was analyzed under 100 °C oven temperature in splitless mode. To determine benzene concentration in the process streams, firstly the calibration curve was created: stock solutions with certain benzene amount were prepared and a linear curve was drawn between the amount of benzene ($\text{g}_{\text{benzene}} / \text{total solution}$) and the area determined in the GC-chromatogram. According to the relationship, the benzene concentration in liquid product phase was determined and the following expression was used to determine benzene conversion:

$$\text{C}_6\text{H}_6 \text{ Conversion \%} = \frac{\text{Inlet}_{\text{C}_6\text{H}_6} - \text{Outlet}_{\text{C}_6\text{H}_6}}{\text{Inlet}_{\text{C}_6\text{H}_6}} \times 100 \quad (4.7)$$

4.4.5 Pressure-Drop Measurement

To examine the influence of removal process on filtration efficiency, pressure-drop tests were performed for fresh and spent filter-based materials. As shown in Figure 4.8, in this system the pressure-drop values across discs were determined from the pressure difference at the inlet and outlet flows to the filter samples.

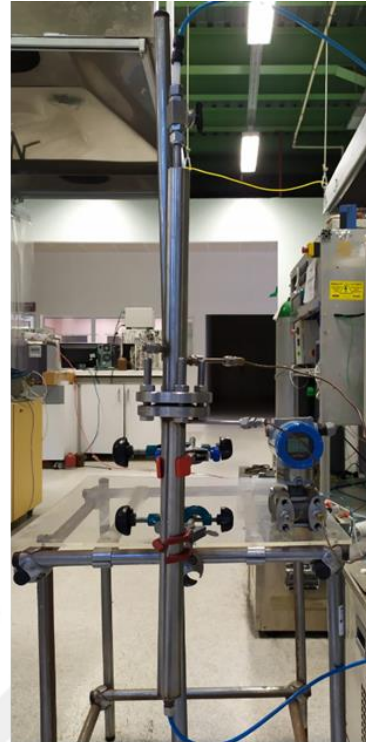
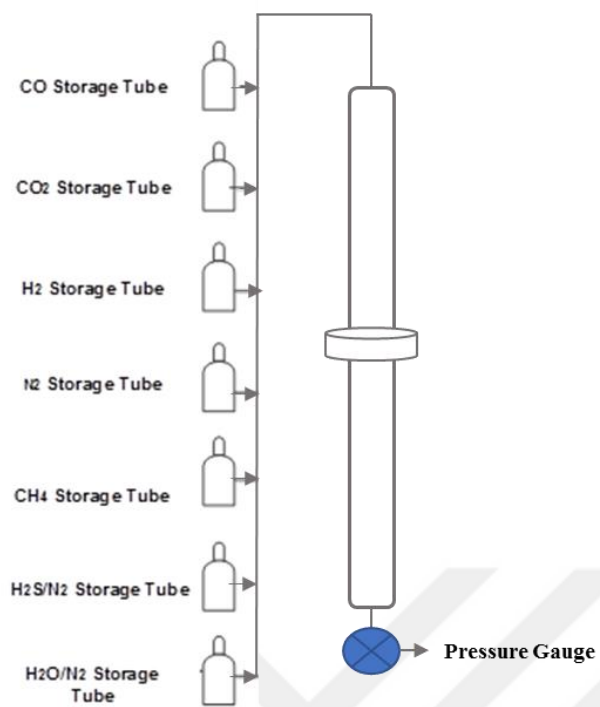


Figure 4.8: Experimental set-up for pressure-drop measurement

5. RESULTS AND DISCUSSION

5.1 Utilization of Zn_2TiO_4 in Desulfurization

Commercial zinc orthotitanate (Zn_2TiO_4 , ZT_c) was utilized as an adsorbent for hot gas desulfurization with the assistance of optimization process conditions, which affected mass transfers between boundaries during the sulfur capture. Primarily, external mass transfer limitation was examined by varying gas velocity and then the relationship between product layer diffusion resistance and temperature was interpreted. Furthermore, kinetic behavior due to the temperature was also analyzed using deactivation model. Secondary, the influence of hydrogen, water vapor and gasification atmosphere on the desulfurization activity of Zn_2TiO_4 was investigated under the as-determined conditions. In addition, the performance data were correlated with the changes in the physicochemical properties of the adsorbent during the reaction using characterization techniques, namely XRD, SEM/EDS and TEM.

5.1.1 Investigation of Diffusion Limitation

5.1.1.1 The effect of fluid velocity

In case of stagnant film model, external resistance to mass transfer takes place in a fluid layer (a hypothetical stagnant film) next to a solid boundary in heterogeneously activated reaction systems. The resistance is attributed the thickness of the film, which is mainly based on fluid linear velocity that is determinative effect on the length of diffusion pathway. Figure 5.1 depicts the effect of the fluid velocity on the boundary layer around a solid sphere. By increasing velocity, the transfer way decreases due to lower film thickness, resulting in efficient external mass transfer. On the other hand, external mass transfer can be correlated with particle size: smaller particles have shorter diffusion pathway in case of similar fluid velocity [165]. According the statements, it can be stated that the external mass transfer resistance can be inhibited using small particles or working at favorable velocities, which is assigned to reaction-limited regime. Therefore, H_2S adsorption features of the zinc titanate samples were explored under different flow rates (1, 2 and 3 L/min) in inert atmosphere ($\text{H}_2\text{S}/\text{N}_2$).

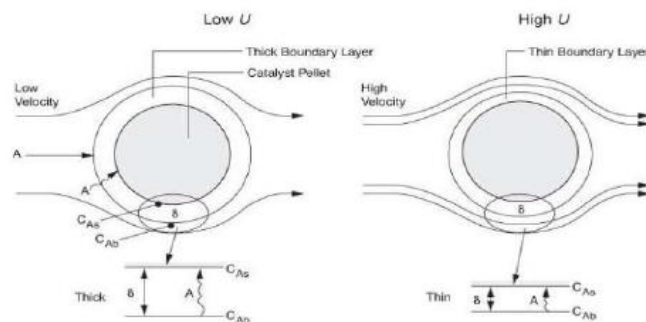


Figure 5.1: Effect of fluid velocity on boundary layer of solid sphere

Figure 5.2 illustrates the effect of fluid velocity on desulfurization performance of ZT_c adsorbents. Clearly, ZT_c exhibited remarkable desulfurization activity under all rate values that the H_2S conversion was close to 100% in the desulfurization runs for 5 h. It can be stated that the reaction rate was independent of the velocity, revealing the absence of any external mass transfer resistance for this range. In addition, the flow rate of 2 L/min was determined as the most convenient point in subsequent studies.

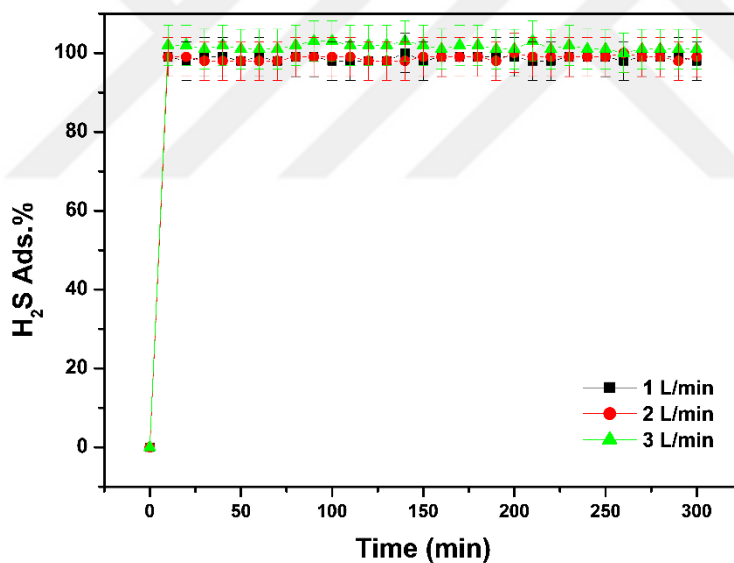


Figure 5.2: Desulfurization performance curves at different flow velocities

5.1.1.2 The effect of temperature

In adsorptive desulfurization, surface reaction can be explained by a Langmuir–Hinshelwood single-site mechanism for which the overall rate coefficient is a function of temperature and diffusion. At sufficiently high temperatures within the thermodynamic boundaries, the observed global reaction rate gets close to the intrinsic reaction rate. That is, when the temperature is sufficiently high, the weak sulfur capture can be related to diffusion limitation [150, 166]. This section therefore presents the

effect of temperature on desulfurization in the presence of zinc titanate. For that, the experimental studies were conducted under three different temperatures (450, 600 and 750 °C) and the results were presented in Figure 5.3.

At early stages of reaction, H₂S conversion was close to 100%, without any dependance on the temperature. At the end of 5 h, the desulfurization efficiency decreased to 41% and 28% at 600 and 450 °C, respectively while it remained constant, around 100% at 750 °C. The enhancement of the desulfurization rate with temperature agrees with thermodynamic behavior that promotes rapidly reaction between Zn-based adsorbent and H₂S due to low activation energy [167, 168]. On the other site, the possible reason for the poor performances at low temperature might be restricted diffusion through external product layer which is attributed to ZnS sheet formed by a diffusion-reaction mechanism. According to the mechanism, sulfur diffuses from the bulk fluid-adsorbent interface into the ZnS/ZnO interface. Reaction occurs at the unreacted site, thereby the product layer (ZnS) thickness increases from the inner site out. Furthermore, during the process Zn²⁺ and O²⁻ ions diffuse through the active external interface [155]. Due to the outworth growth behavior, the reaction can be affected by atomic inter diffusion. The transfer mechanism is expressed by Kirkendall effect which is a well-known phenomenon resulting from the difference in intrinsic diffusivities of chemical constituents in case of solid solution. In other words, due to the product layer the balance between diffusion velocities of S²⁻ and Zn²⁺ is disturbed and the individual rates are decreased, resulting in decreased desulfurization efficiency [169, 170]. According to the statements, the reaction was diffusion limited between 450 and 600 °C and became surface-reaction limited at 750 °C. It can be deduced that during desulfurization on the zinc titanate the product layer diffusion resistance can be eliminated above 600 °C by minimized Kirkendall effect, which is attributed to easy diffusion of the reactants.

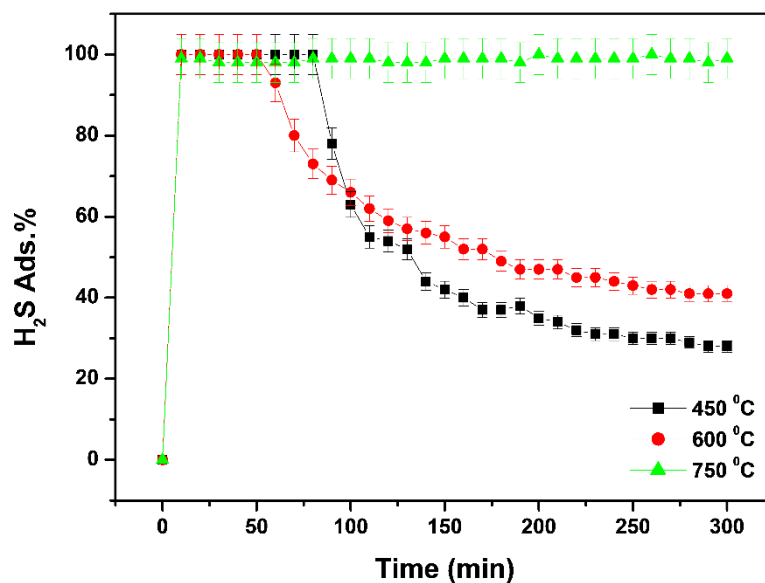


Figure 5.3: Desulfurization performance curves at different temperatures

The structural properties of the as-synthesized and sulfured at 750 °C adsorbents were examined by XRD and the patterns were shown in Figure 5.4. The major diffraction peaks matched well with zinc titanate (Zn_2TiO_4) phase (JCPDS 19-1483) in terms of the fresh and saturated samples, indicating high stability in the presence of H_2S . As reported in international center for diffraction data (PDF 65-1691), ZnS shows a diffraction pattern at 2θ values of 28.5° , 33.1° , 47.4° , 56.3° , 69.4° and 76.7° . Herein, the XRD peak at 2θ values of 47.4° can be considered as the distinct peak for ZnS since the others coincide with the characteristic zinc titanate peaks. Regarding the results, ZnS phase was observed for the samples used at 450 and 750 °C due to the chemisorption of H_2S . Furthermore, at 750 °C the main peaks showed slightly higher intensity than that of 450 °C, indicating that some unstable zinc titanate species such as $\text{Zn}_2\text{Ti}_3\text{O}_8$ in the adsorbent were transformed into Zn_2TiO_4 phase with effective thermal treatment (750 °C).

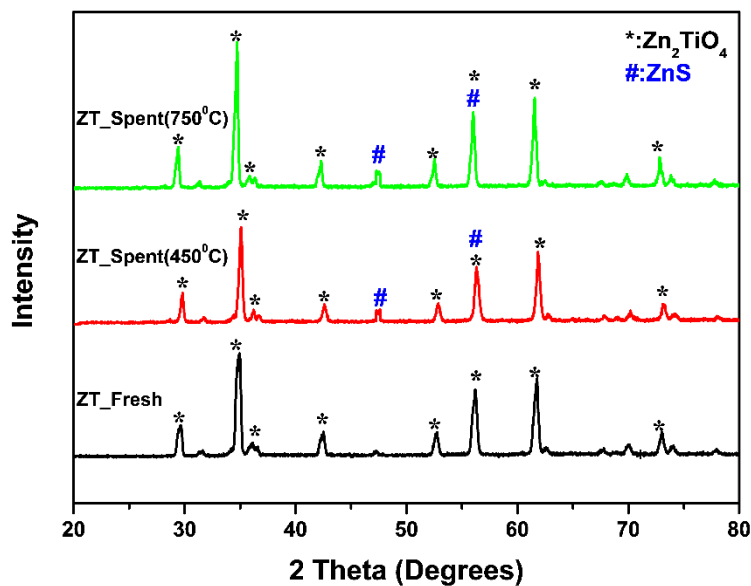


Figure 5.4: XRD patterns of spent ZT_c adsorbents at different temperatures

In Figure 5.5, SEM images of the fresh and used adsorbents at 450 and 750 °C were depicted with surface compositional analysis. Clearly, the non-sulfured zinc titanate sample had a relatively uniform grain size distribution as compared to the sulfured samples. The fresh ZT_c sample seems to have porous sphere-like morphology. During high temperature desulfurization, sintered regions became worth of attention and the stacking particles were attributed to the sintered ZnS agglomerates [154]. Interestingly, channelings appeared as the agglomerated lumps at 750 °C. The observations related to the spent adsorbents could be supported with the results of TEM analysis (Figure 5.6). The corresponding images of the sulfured ZT_c samples dedicated that the particle size was greater at 450 °C than that of 750 °C, providing the product layer formation on the surface with higher ratio. In other words, it can be confirmed that H₂S adsorption was less affected by diffusion limitation at 750 °C. In addition, this easy transfer of the reactants into the unreacted core can be ensured with porous structure after desulfurization at 750 °C.

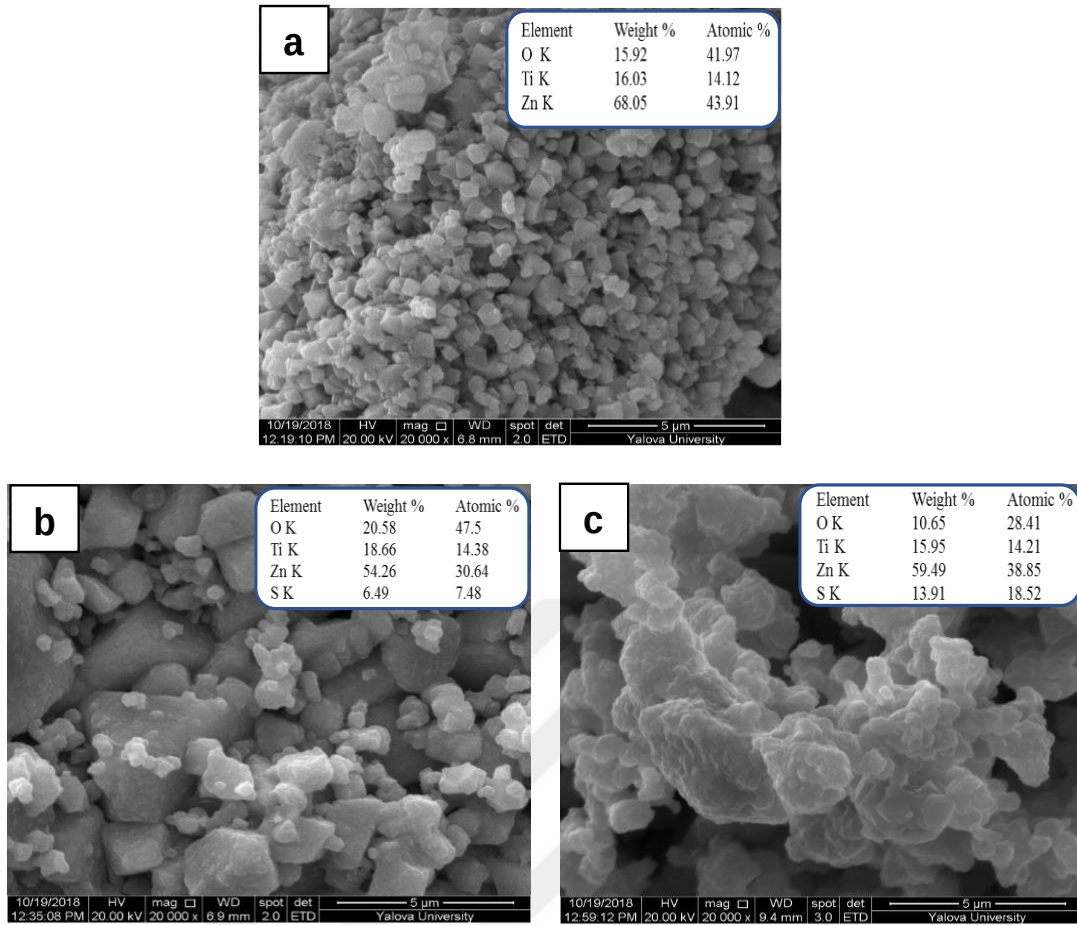


Figure 5.5: SEM-EDS results fresh (a), spent at 450 °C (b) and, spent at 750 °C (c)

As observed in EDS analysis (Figure 5.5 & Table 5.1), the surface Zn/Ti ratio for the fresh and sulfured sorbents at 450 and 750 °C were 3.11, 1.06 and 1.37, respectively. This shows the relative concentration of titanium on the surface increased during desulfurization. Although the desulfurization activity at 450 °C was quite poor than that of 750 °C, the external surface layer of the adsorbent sulfured at 450 °C had higher S/Zn ratio than that of at 750 °C. The result indicated higher amount of sulfide accumulation on the surface. On the other hand, oxygen content of the utilized sample at 450 °C was higher, expecting the unconverted ZnO regions into the external sulfide layer. Additionally, ideally Zn/(O+S) ratio of the external surface should be close to 1, resulting effective utilization range of the active sites under 750 °C with negligible diffusion limitation. It can be therefore stated that desulfurization reaction on Zn sites is significantly influenced by the diffusion as a function of temperature. Similar statement was reported by Bezverkhyy et al. [169].

Table 5.1: EDS analysis of ZT_c adsorbents

Element	Fresh adsorbent	Desulfurization (450 °C)	Desulfurization (750 °C)
O	0.96	3.10	0.60
Ti	0.32	0.94	0.73
Zn	1.00	1.00	1.00
S	0.00	0.49	0.39
Ti/Zn	0.32	0.94	0.73
S/Zn	-	0.49	0.39
(S+O)/Zn	0.96	3.59	1.00

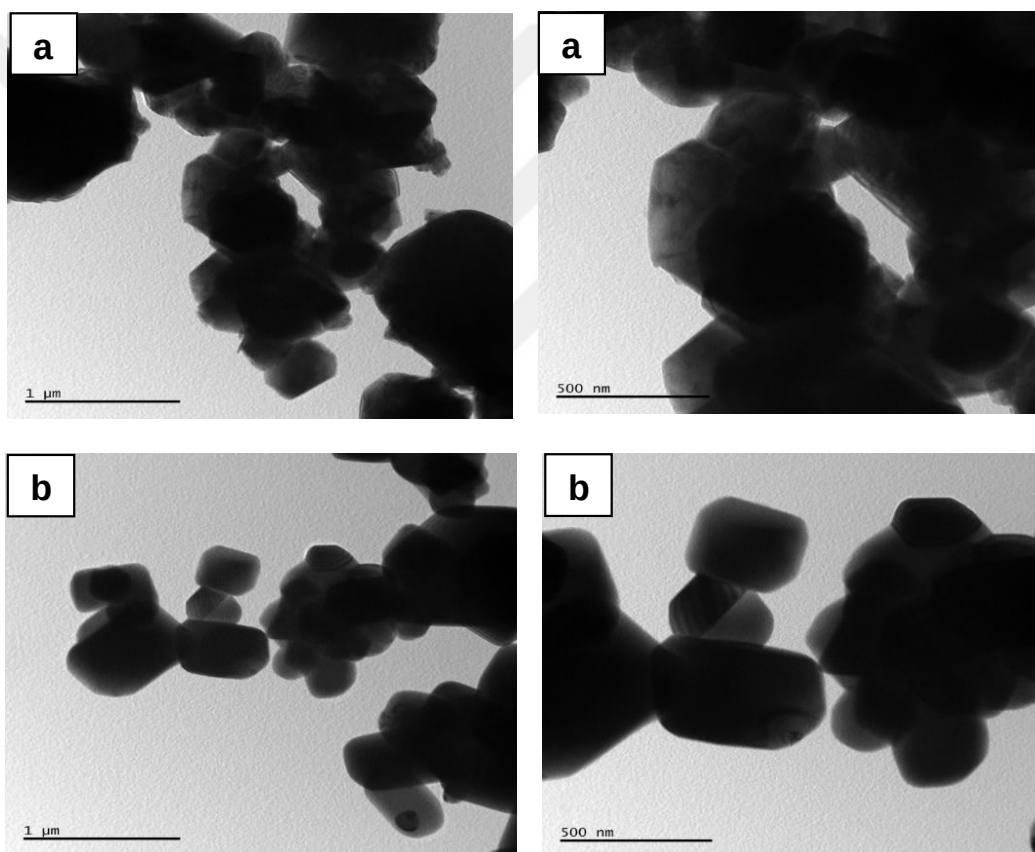


Figure 5.6: TEM images of spent ZT_c adsorbent at 450 (a), and at 750 °C (b)

5.1.1.3 Deactivation model

Another positive effect on H₂S adsorption is to enhance the diffusion rate of H₂S through adsorbent surface by thermodynamically promoting the sulfur bond on metal oxides at a certain temperature. The kinetics of the related sulfurization reaction could be illustrated by using deactivation model in the following equation [5];

$$-\frac{da}{dt} = k_d \cdot c \cdot a \quad (5.1)$$

When the concentration of H₂S was maintained as constant, the equation (5.1) transforms as follows:

$$-\frac{da}{dt} = k_d \cdot a \quad (5.2)$$

Then, the equation (5.2) was integrated:

$$a = a_0 \cdot e^{-k_d t} \quad (5.3)$$

where a is the ratio between reaction rate at certain time (t) and the reaction rate on a solid, t is adsorption time (min), and k_d is considered as deactivation rate constant (min⁻¹).

As a boundary condition, molar flux on the adsorbent surface equalizes the reaction rate on the surface,

$$-F \frac{dC}{dW} = -a \cdot k \cdot c = r_d \quad (5.4)$$

where F is the volumetric gas flow rate, C is the H₂S outlet concentration, W is the adsorbent rate and k is the initial adsorption rate constant. When the diffusion rate in the product layer controls the overall reaction, where the reaction rate constant (k_r) >>> mass transfer coefficient (k_c), k is considered as k_c . In this point, the reaction is expressed as follows:

$$-F \frac{dC}{dW} = -a_0 \cdot e^{-k_d t} k_c \cdot c \quad (5.5)$$

Assuming $a_0 = 1$ at $t = 0$, the equation (5.4) becomes;

$$\ln \left[-\ln \left(\frac{C}{C_0} \right) \right] = \ln \left(\frac{k_c W}{F} \right) - k_d t \quad (5.6)$$

Figure 5.7 presents the change of $\ln(-\ln(C/C_0))$ with time for the H_2S adsorption at 450, 600 and 750 °C. It was observed that the 100% of the removal efficiency took place at the early stage of the chemisorption. After 50 minutes, the H_2S conversion significantly decreased at 450 and 600 °C whereas it declined at 750 °C in a slight way. This greater H_2S conversion could be explained by more unrestricted flow of the gas mixture over and through the adsorbent, providing high contact area between the gas mixture and the adsorbent at the high temperature. For the improved adsorption, another possible reason could be negligible product layer formation. In other words, at low temperatures ZnS produced via the outward growth mechanism could cover the active surface of the adsorbent, resulting in decreased chemisorption. It can be stated that the product layer formation on zinc titanate could be limited with temperature due to the inward growth mechanism during the desulfurization.

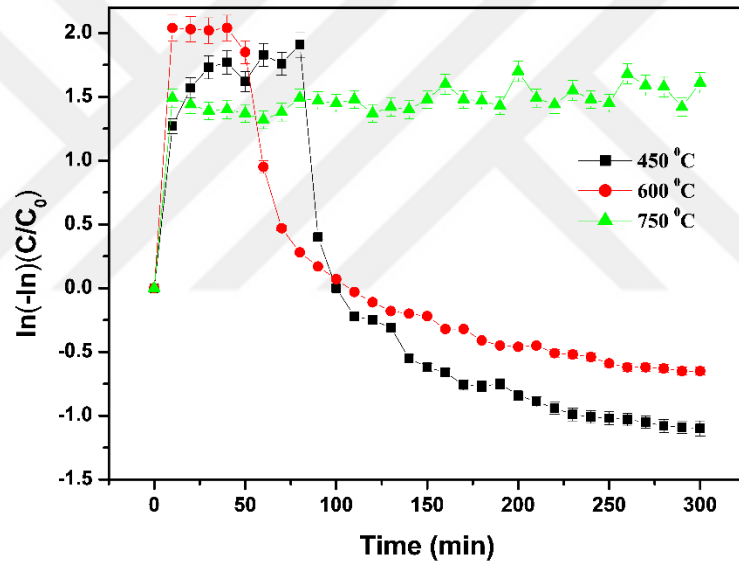


Figure 5.7: Curves of $\ln[-\ln(C/C_0)]$ versus time

On the contrary, it is well known that high temperature greatly enhances diffusion rate in adsorptive desulfurization. To observe this phenomenon, mass transfer coefficient (k_c) and deactivation rate constant (k_d) for all chemisorption temperatures were calculated by using the equation obtained from the plots in Figure 5.8. For the values, the related plots were established at the region where the H_2S conversion had a steady behavior after a sharp activity drop driven by the product layer formation. In other words, the chemisorption performed under internal diffusion limitation. The data fitting functions and regression coefficients were presented in Figure 5.8.

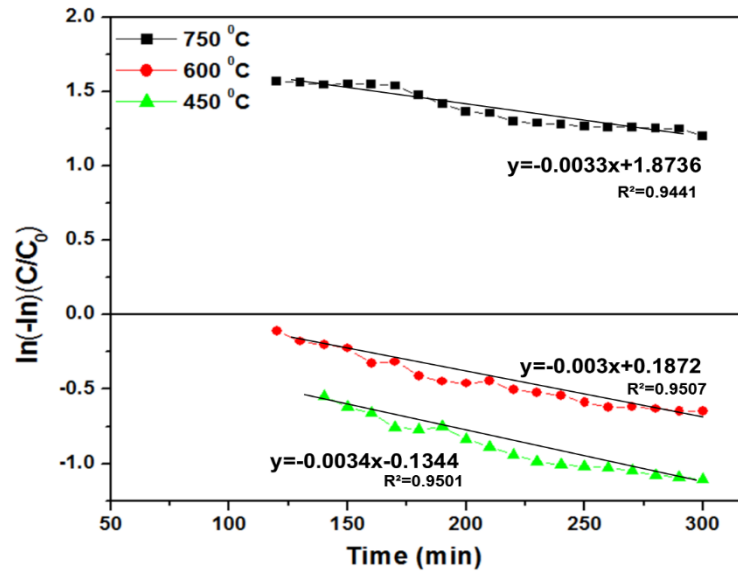


Figure 5.8: Data fitting curves at different temperatures

In Table 5.2, all deactivation rate constants remained constant, suggesting similar desulfurization efficiency were observed in steady state conditions. According to the dependency of mass transfer coefficients with temperature, it could be confirmed that the desulfurization might not be inhibited by the product layer. Therefore, it was concluded that the desulfurization on Zn_2TiO_4 at 750 °C was kinetically controlled with a lesser degree of diffusion resistance through the product layer formation. Similar result was observed by Guo et al. [167] and they demonstrated that the effect of product layer diffusion resistance on the desulfurization of Zn-Mn oxide could be eliminated by increasing the temperature to relatively higher levels, namely to around 650-750 °C [167].

Table 5.2: Mass transfer coefficients and deactivation rate constants

Temperature (°C)	Mass transfer coefficient (k_c , L/g.min)	Deactivation rate constant (k_d , min ⁻¹)
450	0.874	0.0034
600	1.206	0.0030
750	6.510	0.0034

5.1.1.4 Effects of reaction components

H₂S removal performances were measured at different reaction atmospheres, namely reducing, oxidizing and gasification atmospheres. The calculated conversions via H₂S chemisorption under different reaction atmospheres were given in Figure 5.9. The downward trend in desulfurization performance was more significant in the presence of H₂. In this atmosphere, H₂S chemisorption rate reached to zero after 250 minutes, while %94 and 50% of inlet H₂S was captured on zinc titanate in inert and gasification environments, respectively.

For gas mixture, the degree of the reducing can be calculated, as follows:

$$\text{Degree of reduction of a gas mixture} = \frac{\%(\text{CO}) + \%(\text{H}_2)}{\%(\text{CO}) + \%(\text{H}_2) + \%(\text{CO}_2) + \%(\text{H}_2\text{O})} \quad (5.7)$$

The reduction degree of the gasification atmosphere was calculated as 0.6 and the value was determined as 1.0 for inert environment due to the absence of any oxidation agents such as H₂O or CO₂. It is known that hydrogen reduces Zn-Ti-O and ZnO solids at the temperatures above 600 °C [171]. Therefore, it can be stated that when the reducing degree of the reactive gas is high, the loss of active adsorbent sites occurs more rapidly through the reduction of ZnO, resulting decreased performance with higher rate. On the other hand, close to 100% conversion was observed initially for both inert and reducing atmospheres, whereas the reaction started with low conversion values in the case of water vapor and it proceeded with a steadily decreasing trend. Since water vapor is a reaction product, it is thermodynamically reasonable to have a lower initial conversion when compared to the inert and the reducing atmospheres. Furthermore, the poisoning effect of water vapor was claimed by Lew et.al [171]. Two types of sites were proposed; (i) easily reducible but prone to the poisoning by water vapor and (ii) less reactive one but not susceptible to be poisoned by water vapor. In line with this claim, herein it can be stated that zinc titanate has the two different water-induced active sites, resulting that its H₂S capture activity sharply decreased at first, then the trend became smooth in the presence of steam.

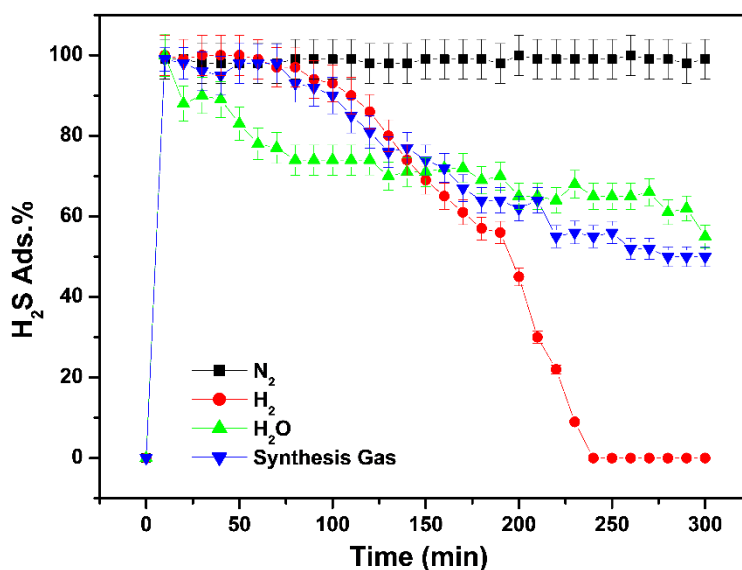


Figure 5.9: Desulfurization performance curves at different gas compositions

Phase analysis of the fresh and spent adsorbents under different atmospheres were performed by XRD and the related patterns were given in Figure 5.10. The loss of characteristic Zn_2TiO_3 peaks was quite remarkable for the spent samples from H_2S chemisorption in reducing atmospheres. TiO_2 phases were well separated at 2θ values of 25.28° for anatase and 27.44° for rutile for the spent sample under 20% H_2 in N_2 mixture.

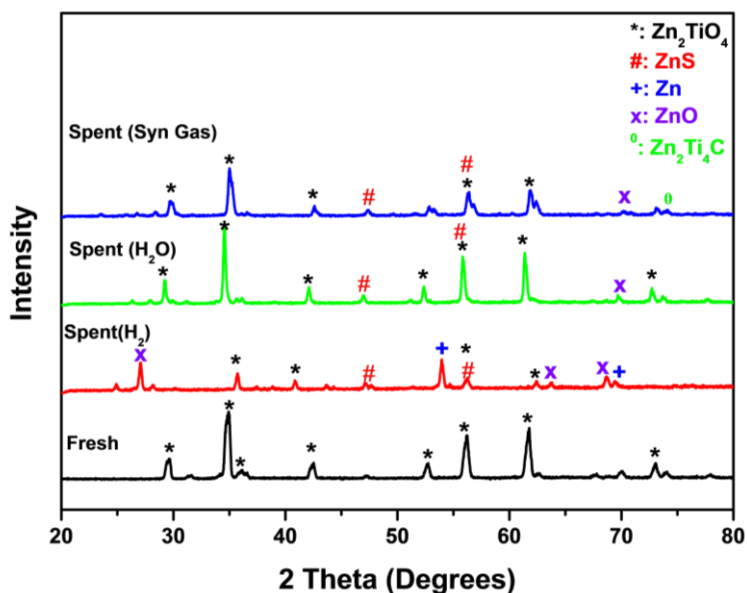


Figure 5.10: XRD patterns of spent ZTC adsorbents at different environments

This is reasonable since the reduction of zinc titanate to metallic Zn and TiO₂ occurs at high temperatures, namely above 650 °C, under the extreme reduction atmospheres as given below:



The distinct XRD peak at 2θ value of 47.4° indicating ZnS was clearly observed for all sulfured samples. The sample exposed to 1% water vapor in N₂ was seen to keep the crystalline Zn₂TiO₄ phase during desulfurization, supporting the fact that water vapor was responsible for poisoning the active sites without any kind of reduction.

This part can be concluded as that for sufficient H₂S adsorptive removal Zn₂TiO₄ should be performed under gas velocity of 2 L/min at 750 °C due to the fact that the conditions promote limited product layer diffusion resistance and improved kinetic behavior. Although Zn₂TiO₄ could be also utilized under gasification conditions, its resistance to oxidant agents should be improved for long-term applications. Therefore, the further experimental part focused on the improving the efficiency of zinc titanate in gasification environments by doping with copper.

5.2 Development of Cu-ZT adsorbents

In this section, copper-incorporated with zinc titanates in different Cu/Zn weight ratios were synthesized by co-precipitation method to examine the effect of copper on the desulfurization performance. For that, the performance studies were performed at 750 °C under 2 L/min gas flow by varying the components of reaction environment which were attributed to inert, reducing, and simulated gasification atmosphere. Additionally, the as-synthesized samples were characterized by XRD, XPS, SEM and BET technique, as well as after the desulfurization, the structural and morphological changes were demonstrated with the methods.

5.2.1 Characterization of Cu-ZT adsorbents

The crystalline structure of Cu-ZT samples was studied by XRD analysis and the as-obtained patterns for bare and doped zinc titanates were given in Figure 5.11. In case of pristine ZT, the diffraction peaks were in good agreement with zinc titanate structures: ilmenite-type hexagonal ZnTiO₃ at 33.28°, 41.21°, 49.72°, 53.00°, and 64.20° (JCPDS 26-1500); cubic phase ZnTiO₃ at 35.56° (JCPDS 39-0190); and spinel Zn₂TiO₄ at 57.50° and 62.67° (JCPDS 19-1483). The characteristic peak of rutile TiO₂

at 2θ value of 27.5° was also detected with low intensity (JCPDS 89-0555). It can be verified that zinc titanate structures could be fabricated by the co-precipitation followed by calcination at 800°C . On the other side, the addition of copper created new peak at 30.06° which intensified with increasing Cu amount. The crystallinity of the other cubic zinc titanate phase with distinctive peak at 35.56° also improved with dopant and the peak was splitted with higher Cu ratio. The results show the formation of cubic and hexagonal ilmenite ZnTiO_3 was promoted in terms of Cu-doped ZT adsorbents. Moreover, the intensity of the TiO_2 (rutile) diffraction peak at 27.5° increased, besides the intensities of Zn_2TiO_4 . The changes can be imputed to the reaction mentioned below:

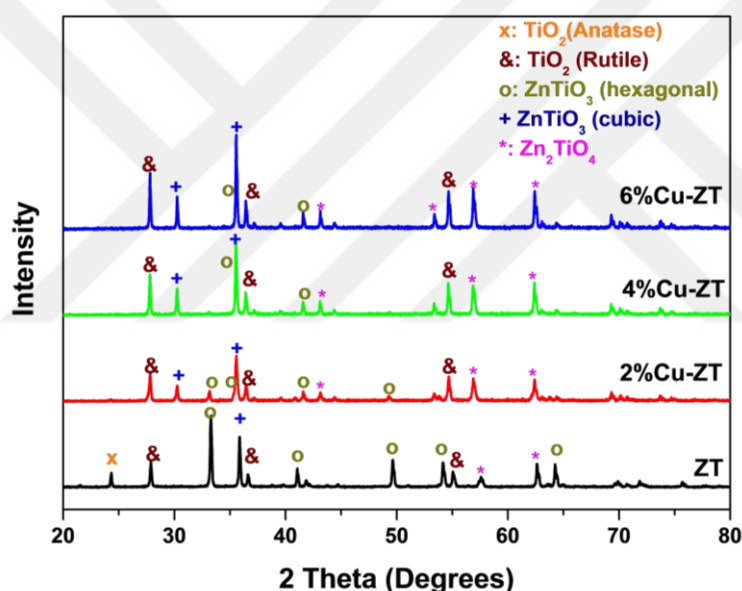
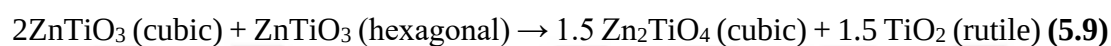


Figure 5.11: XRD patterns of ZT and Cu-ZT adsorbents

Considering the reaction generally takes place over 900°C , it can be deduced that Cu doping might induce the stability of ZnTiO_3 and facilitate the formation of more stable Zn_2TiO_4 phase, herein. Additionally, the absence of the (331) reflection at 2θ value of 47° in all doped samples could be attributed to the presence of the inverse spinel structure of $\text{Cu}_x\text{Zn}_{2-x}\text{TiO}_4$ [172]. However, the $\text{Cu}_x\text{Zn}_{2-x}\text{TiO}_4$ phase could not be detected, as the distinguish of the cubic Zn_2TiO_4 , hexagonal ZnTiO_3 and spinel $\text{Cu}_x\text{Zn}_{2-x}\text{TiO}_4$ phases was difficult due to their overlapping XRD peaks ranging in a very narrow band. On the other hand, the formation of single CuO phase with

monoclinic structure (JCPDS-05-0661) were not observed as evidenced from the absence of its characteristic peak at 2θ value of 32.47° (110), reflecting successful incorporation of copper into the spinel or ilmenite phase of zinc titanate.

In order to examine the effect of desulfurization on the crystal phases, the spent adsorbents (ZT, %2Cu-ZT & %6Cu-ZT) in H_2 -included atmospheres were characterized by XRD (Figure 5.12). After H_2S adsorption, the $ZnTiO_3$ peaks at 2θ values of 30.06° , 35.56° , and 35.74° disappeared while the intensities of rutile TiO_2 peaks at 2θ value of 27.5° , 36.66° , 41.57° and 54.63° were concurrently ascended. Furthermore, the presence of ZnS peaks was observed at 2θ values of 28.5° , 47.4° and 56.3° [173, 174]. These results indicate the formation of ZnS and TiO_2 by the reaction between H_2S and zinc titanates and the relevant reactions can be summarized as follows:

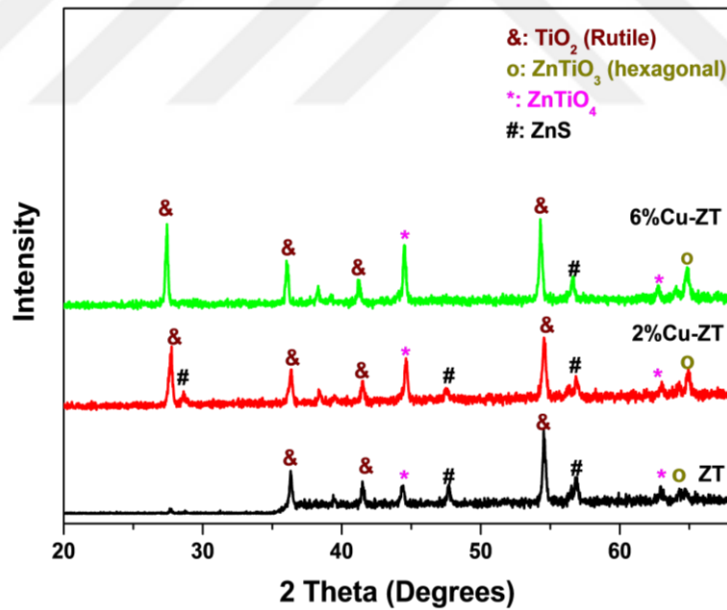
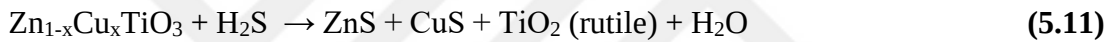


Figure 5.12: XRD patterns of spent ZT and Cu-ZT adsorbents under H_2 flow

The surface areas of ZT and Cu-doped ZT adsorbents were arrayed as follows:

$$2\%Cu-ZT (3.41 \text{ m}^2/\text{g}) > 4\%Cu-ZT (2.54 \text{ m}^2/\text{g}) > 6\%Cu-ZT (1.99 \text{ m}^2/\text{g}).$$

This could be due to the blockage micropores with dopant. Interestingly, the area of ZT increased with the addition of 2% Cu, while it decreased by adding copper higher

than 2%. The decrease could be due to the precipitation particles with high particle size above 2% concentration of the dopant atoms. In addition, the areas of zinc based materials are agree with the study conducted by Lew et al. [154], where zinc titanium oxide solids have total surface areas of around 2-4 m²/g with up to 65 mol % TiO₂.

The morphology and chemical composite of ZT and 6%Cu-ZT samples were analyzed by SEM images and EDS results. Figure 5.13a-b displayed the images of the as-prepared adsorbents. The materials showed well-developed crystalline morphology which assembled by agglomerated small individual crystals. The images were attributed to as eroded sponge shapes with small open spaces and larger voids in 2-4 micron diameter for the fresh adsorbents. Thus, it was suggested that with the doped of 6% copper, the morphological properties of the bare ZT did not change. The macro-porous structures of the adsorbent grains could eliminate external transfer limitation, resulting in high sulfidation activity. On the other hand, the 6%Cu-ZT sample exhibited more dense appearance and less apertures after the desulfurization (Figure 5.13c-d). This could be due to the formation of ZnS and TiO₂ around the unreacted solid core. The EDS results were presented in Table 5.3. It was demonstrated that the molar ratio of O/(Ti+Zn+Cu) of the as-synthesized samples were higher than the theoretical value of 1.5, assuming the formation of ZnTiO₃/Zn_{1-x}Cu_xTiO₃. On the other hand, the high current ratios could be due to the presence of unreacted TiO₂ resulting in O/Ti ratio of 2. Additionally, the relative oxygen concentration increased with dopant, resulting enhanced desulfurization. The result could be supported with XPS analysis.

Table 5.3: EDS analyses of CuZT adsorbents

Element (%molar basis)	ZT	6%Cu-ZT
O	2.00	2.34
Ti	0.77	0.87
Zn	0.47	0.23
Cu	0.00	0.09
O/(Ti+Zn+Cu)	1.61	1.96

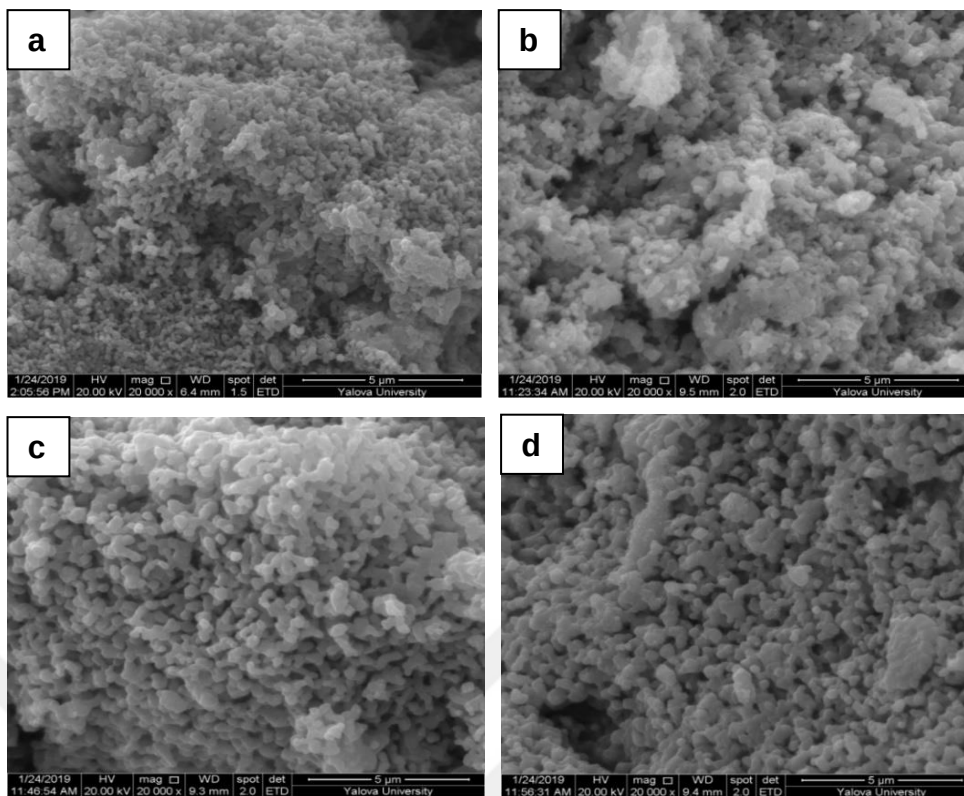


Figure 5.13: SEM images of ZT (a), Cu-ZT (b), spent Cu-ZT in N₂ (c), and H₂ (d)

Figure 5.14 showed the spectra using XPS technique to analyze the valence state of various elements in ZT and 6% Cu-ZT. The related overall spectra were presented in Figure 5.14(e) that showed the binding energies of Zn, Ti and O in ZT, and also observed the presence of Cu peak with the elements for 6%Cu-ZT. In Figure 5.14(a), the Zn spectrums displayed two peaks at ~ 1022 and ~ 1045 eV [185], which correspond to the binding energies of $2p_{3/2}$ and $2p_{1/2}$, respectively. This indicates the presence of oxidation state Zn^{+2} in the zinc-based adsorbents. As can be seen from Figure 5.14(b), the effective binding energies of 458.6 and ~ 465 eV were attributed to $Ti2p_{3/2}$ and $Ti2p_{1/2}$, respectively. Generally, $Ti2p_{3/2}$ spectrum includes two-splitted peak, however herein the second peak was not observed around 457-458 eV. This could be due to the formation of $Ti2p_{3/2}$ with an tetrahedral environment [175]. In the Cu spectrum (Figure 5.14(d)), the “shake-up” satellite peaks between 930 eV and 960 eV were derived from $Cu2p_{3/2}$ species in +2 state [118, 176]. The findings also confirmed the presence of $Cu_xZn_{1-x}TiO_3/Cu_xZn_{2-x}TiO_4$ structures in the 6%Cu-ZT lattice.

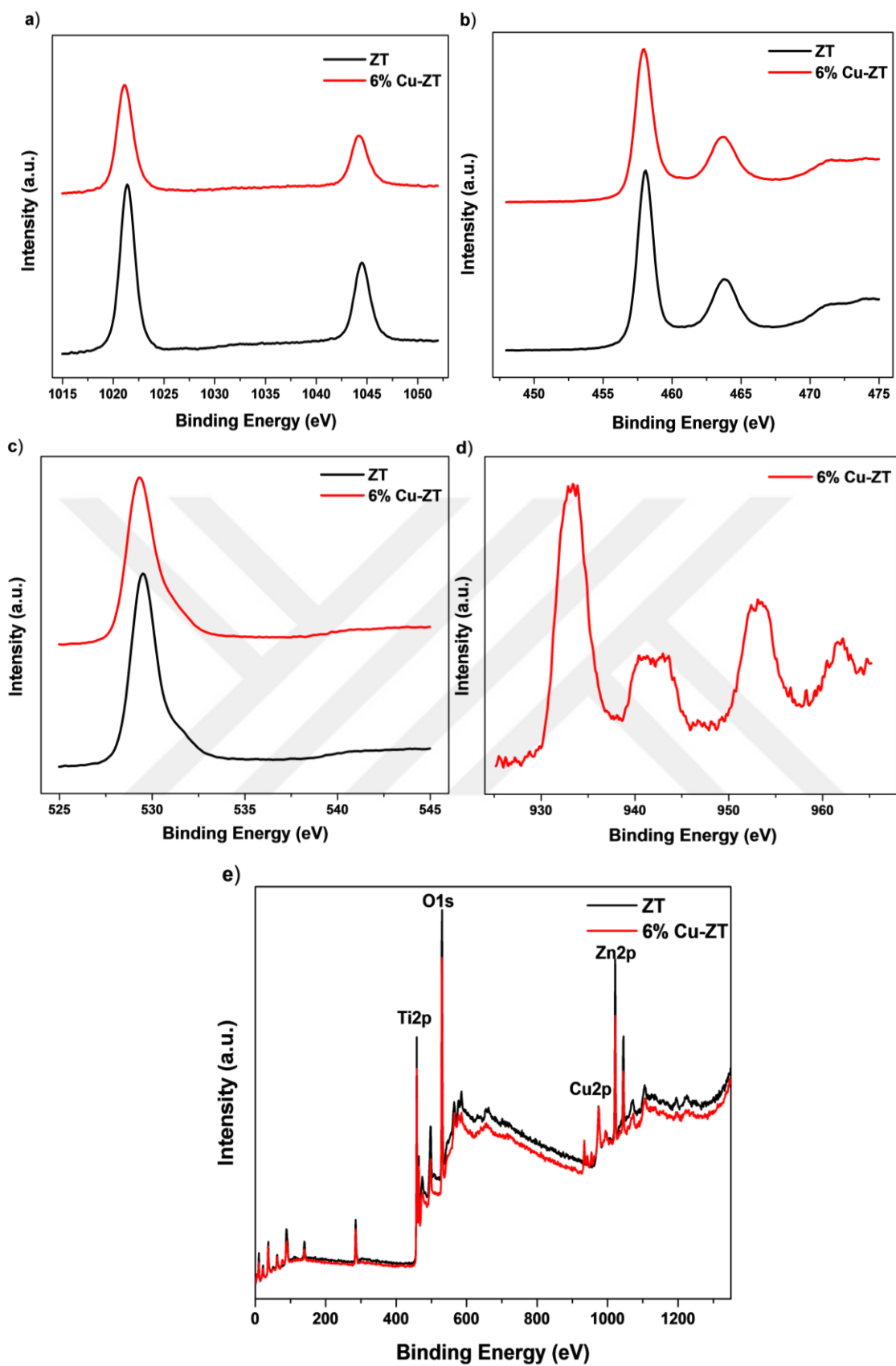


Figure 5.14: XPS spectra of ZT and Cu-ZT: Zn2p (a), Ti2p (b), O1s (c), Cu2p (d), and survey spectra (e)

As observed in Figure 5.15, the main O1s location was 529.6 eV and the other location was observed at around ~531 eV in a shoulder view, which were assigned. The statements were due to the lattice oxygen and surface-adsorbed oxygen [177]. The results could also provide the formation of zinc titanates in rhombohedral ilmenite and spinel type structures [175]. The higher intensity of peak at ~531 eV was observed for 6%Cu-Zt than that of ZT due to the fact that Cu more easily incorporated into the $A_xZn_{2-x}TiO_4$ solid solution [172]. Therefore, the partial incorporation of Cu^{2+} in the $Cu_xZn_{2-x}TiO_4$ framework might be proposed which was not verified through the XRD measurements. In addition, the higher intensity peak related to the oxygen species in 6%Cu-ZT could reflect enhanced adsorption ability with a higher number of defects and vacancies.

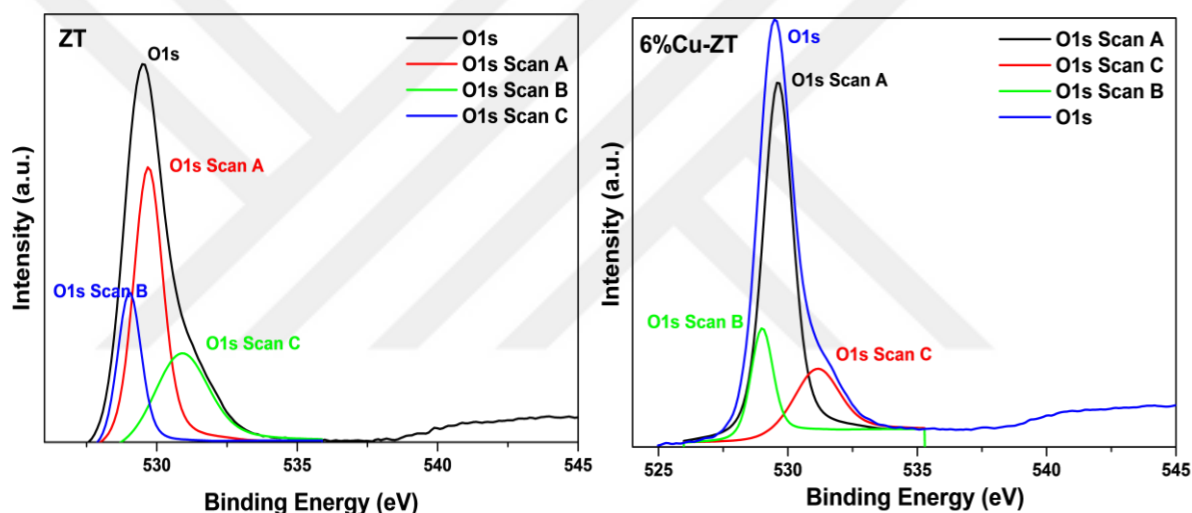


Figure 5.15: O1s spectra for ZT and Cu-ZT in deconvolution

5.2.2 Desulfurization Studies of Cu-ZT adsorbents

Desulfurization performances of zinc titanate adsorbents with different Cu loadings were shown in Figure 5.16. In inert atmosphere, all samples exhibited 100% sulfur removal (Figure 5.16a), while in the presence of H_2 the order of ability over the active materials to capture H_2S for 5 h was: 6%Cu-ZT > 4%Cu-ZT > 2%Cu-ZT > ZT (Figure 5.16b). In the desulfurization activity under reducing atmosphere, the addition of copper had a significant improvement by enhancing the stability: Cu-doped adsorbents lost their activities more slowly than the bare ZT. Considering their durability, it was observed that 2% and 4% doped ZT samples maintained their H_2S removal efficiencies at stable around 100% for 50 minutes, while 6% Cu doped ZT depicted high

performance in two folds time. The enhancement could be due to the increase in the basic character of the adsorbents with copper doping, promoting the chemisorption of acidic compounds like H_2S . This result are in line with the statement presented by Kang et al. [178]. In other words, Cu^{2+} ions could provide to adsorb H_2S with a much lower binding energy than that of Zn^{+2} states, resulting higher capture capacity in the doped-adsorbents. In order to assure this statement, “HSC Chemistry” computational software package was applied to examine desulfurization reactions with ZnO and CuO in the context of equilibrium thermodynamics. The metal oxides were attributed to active sites (Zn^{+2} and Cu^{+2} states) depicted from the XRD results. As shown in Figure 5.17, CuO had higher potential for H_2S adsorption at 700-800 $^{\circ}\text{C}$, indicating that the incorporation of Cu into ZT lattice was beneficial to desulfurization

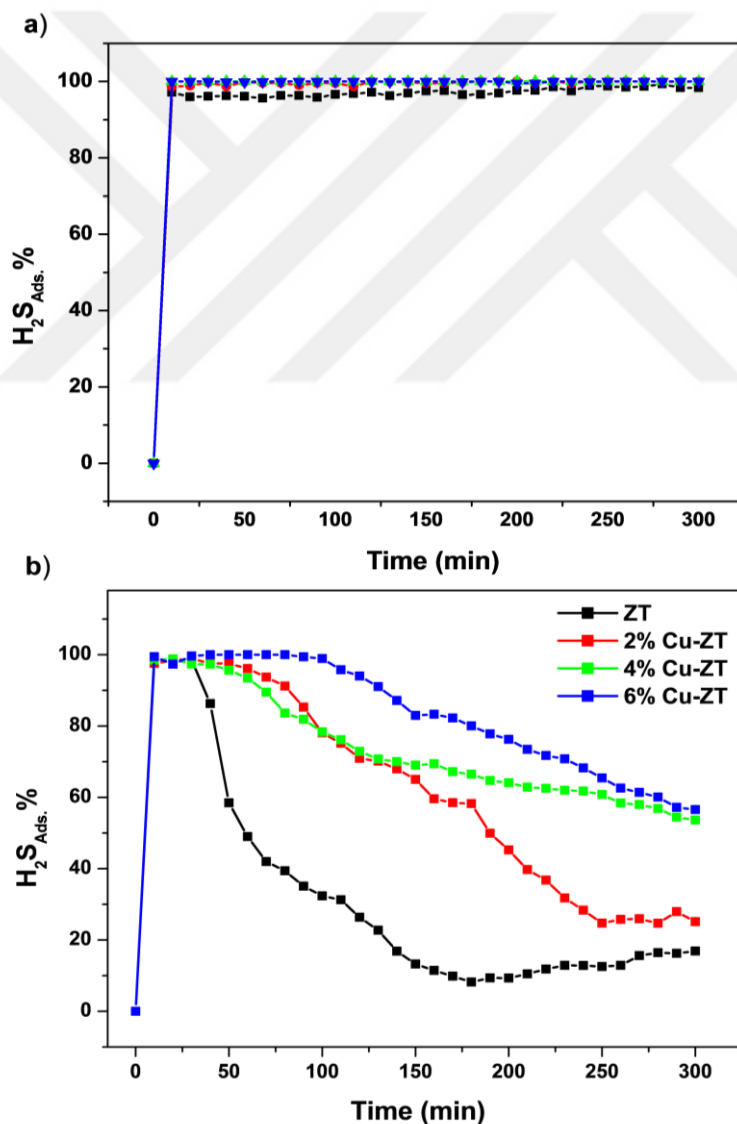


Figure 5.16: Desulfurization performance curves of Cu-ZT adsorbents under N_2 (a) and H_2 flows (b)

It was also observed that the overall trend during the desulfurization in reducing atmosphere is to decrease with time for the as-synthesized adsorbents. As widely known that hydrogen causes the reduction of zinc-based oxides above 600 °C and the Zn-active sites undergoes grain-growth due to the sintering around 700 °C [154], resulting decreased desulfurization efficiency at high temperature. In this study, the grain-growth and the changes in grain shape did not observed in the SEM images. This could be due to the fact that rhombohedral ilmenite and spinel type zinc titanate structures inhibited the sintering of the zinc particles. Therefore, it can be stated that the major impact on decreased activity with time was the transformation of Zn particles to metallic Zn during the reaction in the presence of ZT.

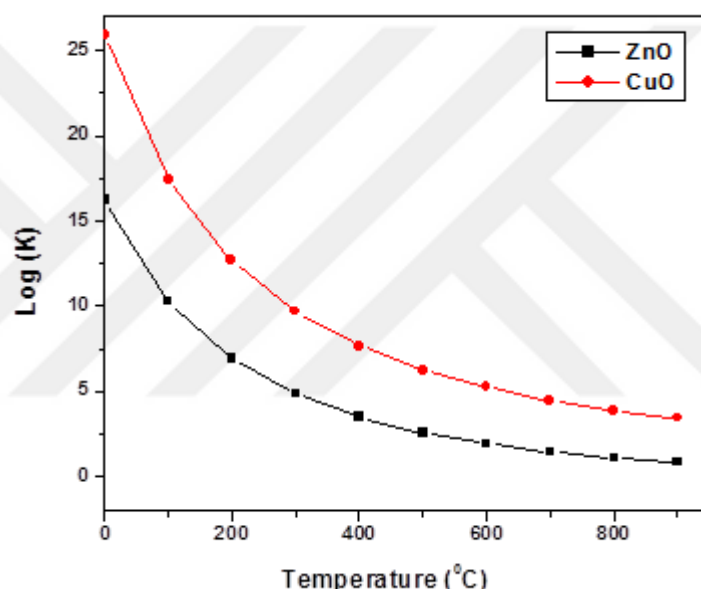


Figure 5.17: Desulfurization equilibrium constants at different temperatures

In terms of Cu-doped ZT, the downward trend could be due to the reduction of Cu^{2+} into Cu^{+1} (Cu_2O) and metallic Cu which were attributed to low activity for high-temperature desulfurization [179]. Considering the ability of the reduced states on sulfur capture and the occurrence of slowly reducing behavior (Figure 5.16b), it could be stated that Cu improved the H_2S removal efficiency of ZT with the proportional to copper amount. The result was supported with the previous studies as follows: Pineda et al. [180] demonstrated that the desulfurization performance of zinc ferrite in the presence of reducer component improved with the incorporation of the adsorbent with Cu ions, resulting favorable H_2S removal with decreased activation energy. Liu et al. [181] presented that the copper loading increased the efficiency of $\text{ZnO-Al}_2\text{O}_3$ on

sulfur capture and the 6 wt.% copper addition resulted in an ultra-deep desulfurization process. Additionally, the enhanced H_2S removal performances of Cu-doped ZT adsorbents in reducing atmosphere could be driven by less diffusional restraints over the adsorbents. The thickness of the product layer creating a diffusional barrier might be lower due the migration of the copper species to the external surface.

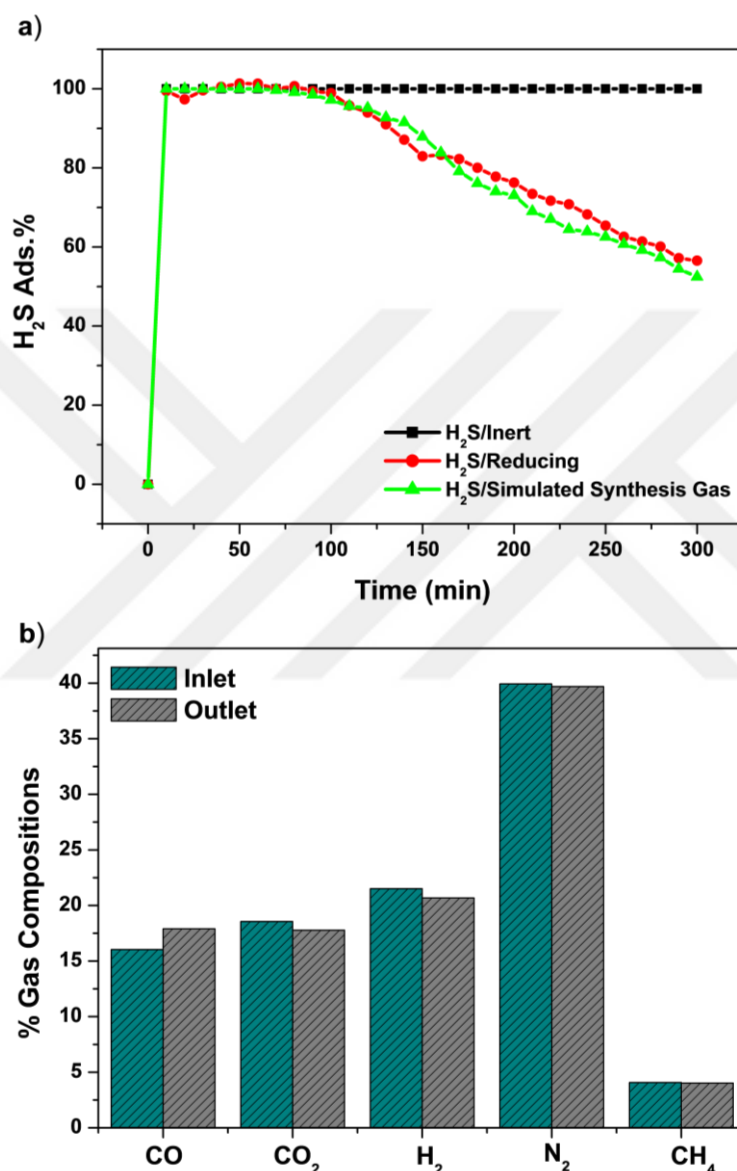


Figure 5.18: Activities of Cu-ZT adsorbent (a) and changes in gas components (b)

The effect of reaction composition was determined by comparing the desulfurization efficiencies under three different environment cases (inert, reducing and gasification) in the presence of 6%Cu-ZT (Figure 5.18a). Under the reducing and gasification atmospheres the desulfurization performances showed obvious decrease and the final sulfur sorption was 54% and 57% under H_2 flow and simulated synthesis gas mixture,

respectively. On the other hand, the variation of gas contents during reaction was presented in Figure 5.18b and it was observed that the amount of CO increased whereas the quantities of CO₂ and H₂ decreased. The result indicated that during the removal process the reverse water-shift reaction was promoted in the following of the reaction:



The product of this reaction, namely steam could be possible reason for low sulfur removal in the simulated gas phase. The poisoning effect was also reported in literature [154]. On the other side, the presence of H₂ resulted decreasing the activity due to low active sites driven by the reduction of the oxide structures. Furthermore, steam was obtained during the metal-based reduction. Thus, similar behaviors could be observed under both the atmospheres.

In overall, this section serves as a synthesis method for spinel-based structure as mixed zinc titanate and Cu-doped the zinc-based samples. Furthermore, the addition of Cu into the zinc lattice enhanced desulphurization activity under reducing and gasification atmospheres due to the segregation of Cu²⁺ to the adsorbent surface in the lower oxidation state, presenting thermodynamically favorable sulfur capture. In addition, 6% Cu-ZT was considered as the most promising one for further studies.

5.3 Investigation of Integrated System Combined Reforming and Desulfurization

In this part, the desulfurization and hydrocarbon reforming stages were aimed to arrange in series during biomass gasification. For that, two catalytic substrate-based calcium silicate filters were prepared: one ceramic filter disc was incorporated with copper-doped zinc titanate by ball-milling process for sulfur removal. Another filter disc was coated with alumina supported nickel particles (Ni/Al₂O₃) by impregnation method for tar degradation. Primarily, hydrogen sulfur removal was evaluated in different environments (inert, reductive, and simulated gasification atmosphere) in terms of the heterostructure including Cu-ZT and ceramic filter. Then, nickel-based filter material was investigated for catalytic methane and benzene degradation in sulfur-free and sulfur-included gasification gas mixture. Secondly, an integrated system was carried out to evaluate the efficiency of two-step removal process, which included the two different active stages for both sulfur and tar removal. In addition,

the characterizations of the as-fabricated samples were carried out by XRD, SEM and FTIR methods and in the integrated system the desulfurization effect was examined by elemental mapping.

5.3.1 Characterization of CuZT/p-CF Composites

The crystal structures of CuZT, CF and CuZT/p-CF composite samples were characterized by XRD analysis (Figure 5.19). As mentioned in the previous section, CuZT showed the diffraction of cubic phase ZnTiO_3 , hexagonal ilmenite phase ZnTiO_3 , Zn_2TiO_4 , TiO_2 as well as the formation of $\text{Cu}_x\text{Zn}_{2-x}\text{TiO}_4$ were observed. In case of ceramic filter material (CF), the major diffraction peaks matched well with wollastonite mineral (CaSiO_3) phase [182]. In case of the XRD patterns of the heterostructure samples new diffraction peaks were not observed, indicating that new crystal structure was not formed after ball-milling process. Furthermore, with increasing CuZT amount in the composite material, the characteristic TiO_2 (around 27.5° and 36.7°) and ZnTiO_3 (30.06°) peaks became clear and there was no shift in main peak positions of the mineral. These results showed that the zinc titanate was successfully incorporated into the host lattice without disturbing the crystal structure of CF during the ball milling process.

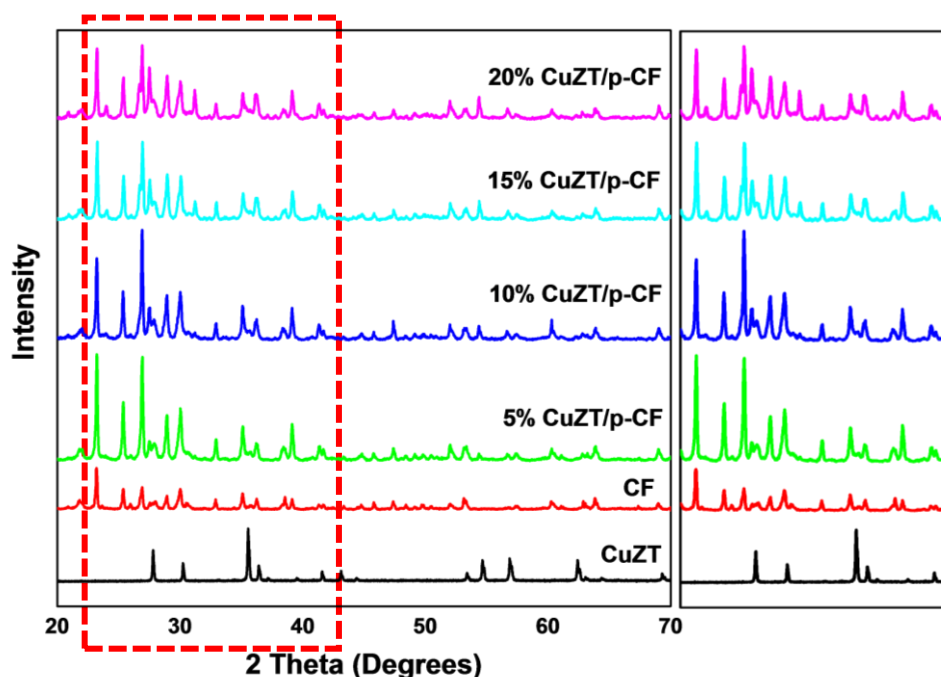


Figure 5.19: XRD patterns of CuZT, CF and CuZT/p-CF composites

The chemical structure of fabricated samples was examined by FT-IR spectra presented in Figure 5.20. In the range of 650-1400 cm^{-1} , the structures of CuZT/p-CF samples were almost identical to that of pristine CF. In case of all samples, the main peak at 902 cm^{-1} corresponded to the stretching of Si-O-Ca, which indicates the formation of calcium silicate [183]. The absorption band at 967 cm^{-1} was attributed to the stretching vibration of silanol groups (Si-OH) cm^{-1} [184], and the Si-O-Si asymmetric and O-Si-O symmetric& asymmetric stretching vibrations were depicted with the peaks at 1060 and 1018 cm^{-1} , respectively [185]. The weak absorption peak at 681 cm^{-1} was also assigned to Si-O-Si symmetric stretching vibrations [185]. After the incorporation of CuZT with the filter material, the new peaks occurred in the range of 720-800 cm^{-1} corresponding to the Zn-O-Ti bond structure in cubic ZnTiO_3 [186]. The results confirm the loading of CuZT in the CaSiO_3 framework in line with XRD results.

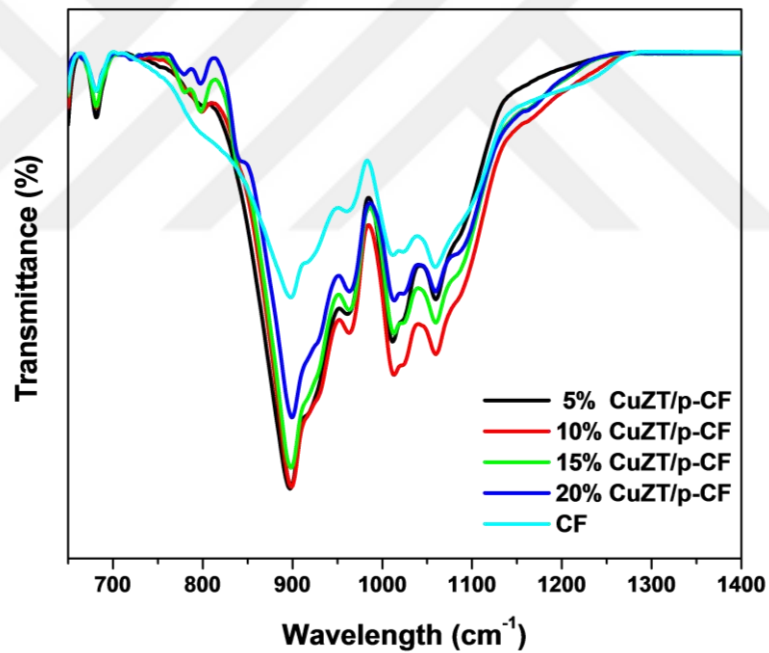


Figure 5.20: FTIR spectra of CF and CuZT/p-CF composites

The morphological properties of CuZT, CF and 20%CuZT/p-CF were ascertained by SEM images (Figure 5.21). In Figure 5.21a, CuZT appeared as severe agglomeration by sphere like particles joining, as mentioned before. Ceramic filter had fiber-like morphology with higher porosity (Figure 5.21b). The results could be supported with the specific surface area of the materials; for 1.99 m^2/g for CuZT and approximately 150 m^2/g for CF. From the images of the composite structure, it was observed that zinc

titanate-based particles were attached on the fibers, indicating that the introduction of spinel substrate into calcium silicate did not destroy the fiber structure of the filter (Figure 5.21c). On the other hand, it could be said that the ball-milling provided the distribution of the CuZT particles on the filter with lower agglomeration efficiency. The distribution might be ascribed to the higher amounts of active centers. The obtained results revealed that the mechanical process provided the formation of smaller CuZT grains on CF corresponding to enhanced utilization efficiency of zinc titanate in 20%CuZT/p-CF for hydrogen sulfur removal.



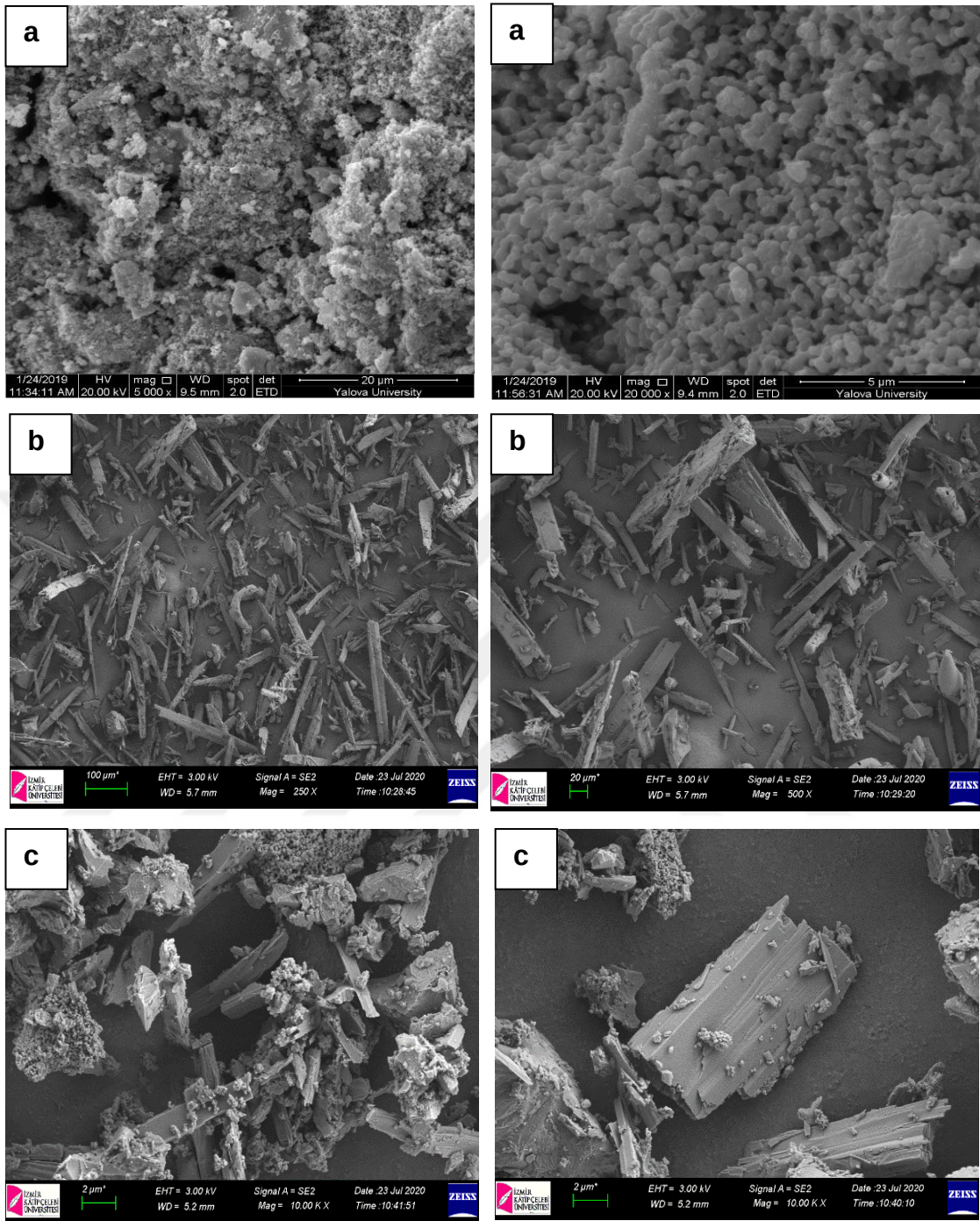


Figure 5.21: SEM images of CuZT(a), CF(b) and CuZT/p-CF(c) samples

5.3.2 Desulfurization Activities of CuZT/p-CF Composites

To investigate the potential application of CuZT loaded ceramic filter disc as an adsorbent at high temperature (750 °C), hetero-adsorptive catalytic degradation of hydrogen sulfur under different environment was employed (Figure 5.22). Figure 5.22a depicts the H₂S removal performances of CuZT/p-CF series under N₂/H₂S environment and the performances of bare CuZT and CF were also shown. While the pristine CF showed the removal efficiency of 86% under inert atmosphere, the value close to 100% was achieved for all CuZT/p-CF hetero structures, demonstrating the fact that the addition of CuZT phase contributed to H₂S adsorption. This could be caused by increasing the basicity of the disc with CuZT that was driven for the adsorption of acidic H₂S. In short words, CuZT showed higher affinity to chemically adsorb H₂S than that of CF due to lower binding energy. In addition, the results revealed that only 5% CuZT addition into CF lattice reached the performance of CuZT, indicating that well-distributed zinc-based particles on the disc lattice improved the area of the active sites for H₂S adsorption.

As illustrated in Figure 5.22b, the removal efficiencies significantly changed under reducing atmospheres as compared to inert environment. The CF showed 20.7% of H₂S chemisorption ability in the presence of hydrogen at the end of 5 hours-time, while all CuZT/p-CF composite adsorbents disclosed higher sulfur removal performance. These values were determined as 21.1%, 25.7%, 28.4% and 48.1% for 5%CuZT/p-CF, 10%CuZT/p-CF, 15%CuZT/p-CF and 20%CuZT/p-CF, respectively. That is to say, all CuZT/p-CF composite adsorbents showed an increase in the removal performance as compared to the bare filter. This could be due to the promoting effect of copper based zinc titanate on sulfur adsorption. The result could be supported with the H₂S adsorption efficiency of CuZT under hydrogen included flow (Figure 4.24b), resulting 56.6% removal value. Furthermore, it was observed that 20%CuZT/p-CF displayed a very close degradation ability to the bare metal-oxide structure. As previous study, the kinetics of H₂S adsorption by copper doped zinc titanate could be explained with a shrinking-core mechanism, which was attributed to that the global reaction was diffusion limited due to a product layer formation on surface. It could be indicated that the dispersion of CuZT on filter material might greatly improve the sulfur diffusion with high surface area, increasing the CuZT effectiveness.

Additionally, CF reached a steady state zone at the early period of the reaction, while the H₂S chemisorption efficiency of H₂S on CuZT did not change until 100 min, then it showed a decreasing trend (Figure 5.22b). It could be therefore indicated that the filter and active phase showed different behavior in the presence of hydrogen. As known, calcium silicate structure easily established hydrogen bonding by force of its silanol groups. It could be therefore stated that the host material preferred to be bounded to hydrogen rather than hydrogen sulfur. The inhibitory effect of hydrogen for CuZT substrate was based on the reduction ability of active sites. Zinc-based phases were reduced at higher temperature than 600 °C, resulting a decrease in the sulfur removal [154]. On the other hand, under hydrogen flow Cu⁺² reduced to Cu⁺¹ and metallic Cu, which had the activity of the hydrogen sulfur adsorption. Furthermore, the reduction of Cu⁺² occurred in slow way [180, 181]. These situations were attributed to the efficiency of hydrogen sulfur adsorption at the end of 5 h. In terms of composite materials, after a drop in the adsorption, the removal efficiency remained stable during the rest of the process time without further activity loss, indicating that the CuZT/p-CF heterostructures acted as both host and catalytic materials in the desulfurization process. In other words, the composites were more stable than CuZT and more active than CF. Therefore, it could be concluded that under hydrogen flow CuZT promoted the adsorption of H₂S on CaSiO₃ due to enhanced resistance against diffusion limitation and limited reduction.

In the case of gasification atmosphere, a similar trend was observed for H₂S removal in H₂ environment. While the pristine filter adsorbed approximately 10% of H₂S, the adsorption efficiencies of composite filters were found to be 10.3%, 22.5%, 26.7% and 39.8% for 5%CuZT/CFD, 10%CuZT/p-CF, 15%CuZT/p-CF and 20%CuZT/p-CF, respectively (Figure 5.22c). In terms of ceramic filter, the loss of activity might be due to higher competition degree between molecules, since CO₂ and H₂O could be easily adsorbed on CaSiO₃ structures [187, 188]. The decrease in the performance could also be ascribed to the possible reduction with oxidant agents (CO and H₂O) as well as hydrogen. On the other hand, in the early stage of reaction, the H₂S removal significantly enhanced with increasing number of active sites into CuZT, while the reduction rate increased with CuZT concentration. This could be attributed to high and fast reduction feature of CuZT in the simulated synthesis gas.

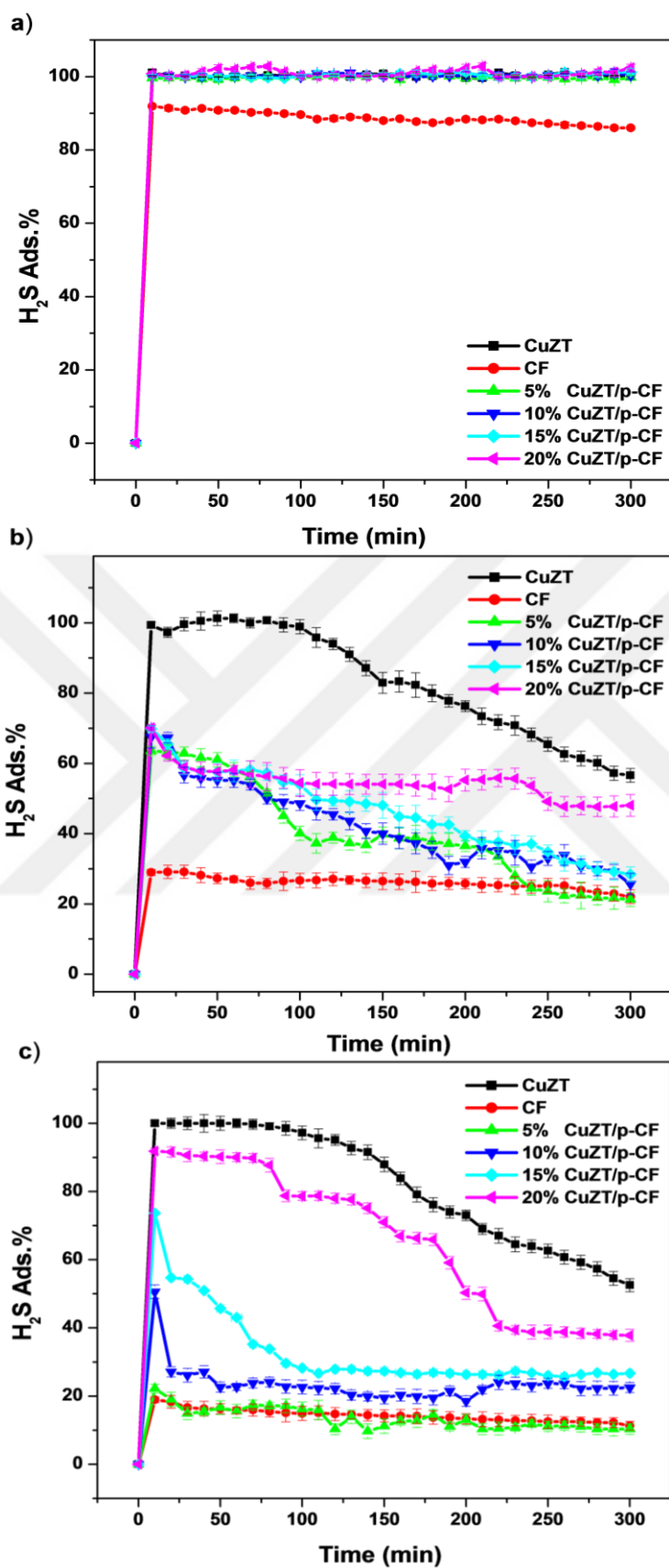


Figure 5.22: Desulfurization performance curves of CuZT/p-CF composites under N_2 (a), H_2 (b) and simulated synthesis gas (c)

In overall, this part highlighted the synergistic effect between CuZT and CF for H₂S removal under inert, reducing and gasification environments. This finding indicated that CuZT/p-CF heterostructure could be a promising candidate as a sulfur adsorbent for biomass gasification system. In addition, the as-prepared 20%CuZT/p-CF sample approached the performance of CuZT (55.9%), resulting the most prominent desulfurization performance and therefore this sample was performed in the further subsequent experiments herein.

5.3.3 Steam Reforming Activity of Ni/Al₂O₃/d-CF

The potential application of Ni/Al₂O₃ impregnated ceramic filter disk (Ni/Al₂O₃/d-CF) as a promising cracking catalyst was examined during gasification process. Before its utilization in the hydrocarbon cracking reaction, Ni/Al₂O₃/d-CF was characterized using XRD method to ensure its crystalline structure (Figure 5.23). In the XRD pattern, the main peaks were attributed to CaSiO₃ phase driven by ceramic filter. Furthermore, the peaks corresponding to NiO were observed at 36.4°, 44.2°, and 63.1° (JCPDS Card No. 47-1049). The other signal was also investigated at 2θ value of 68°, which could be indexed to γ-alumina (Al₂O₃) (JCPDS card 10-0425). The minor peak at 2θ value of 41.68° was characterized by CaO.Al₂O₃ phase (PDF#00-006-0495). This could be due to the strong interaction between calcium oxide and alumina oxide at higher temperatures than 600 °C [189]. The analysis results confirmed successfully doping of nickel oxide and boehmite on the ceramic filter with colloidal impregnation followed by dry impregnation.

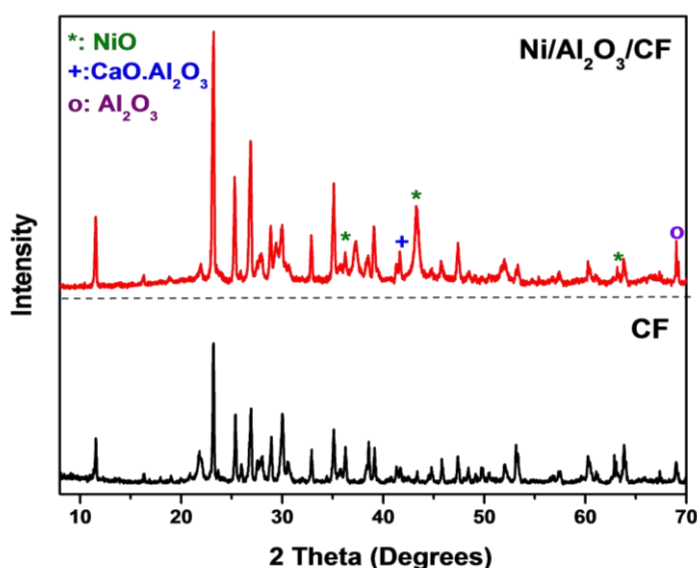


Figure 5.23: XRD pattern of Ni/Al₂O₃/d-CF and CF samples

In order to examine catalytic efficiency of Ni/Al₂O₃/d-CF, steam reforming of methane under simulated synthesis gas was employed in a one-stage reactor system (Figure 5.24). Figure 5.24a displays the performance of the bare CF and Ni/Al₂O₃/d-CF in methane reforming under sulfur-free gasification atmosphere. The pristine filter material showed negligible reforming activity (3%), whereas the nickel based CaSiO₃ filter displayed 80% of methane conversion at the end of reaction. The reflection of the activity was observed as an increase in hydrogen and carbon monoxide concentrations in the reactor outlet gas flow (Figure 5.24b). This implied that in the presence of the coated disk sample the main dissociation reaction of steam methane reforming (Eq. (5.13)) shifted equilibrium to the right side at 750 °C for hydrogen and carbon monoxide production;



The most known reason of catalyst deactivation during carbonaceous substrate cracking is inactive coke deposition on active metal sites that cause a decreasing trend in the conversion efficiency. After 5 h, the change in methane conversion was minimal, indicating that the catalyst structure seemed to be stable during steam methane reforming in the synthesis gas. Thus, it was suggested that Ni/Al₂O₃/d-CF was successful candidate as a catalyst in methane steam reforming in the biomass gasification system.

When H₂S was added into the simulated synthesis gas, the methane conversion decreased to 13% for 1 h and subsequently declined to 4% until 5 h (Figure 5.24c). This could be due to the blocking active nickel sites by H₂S in line with desulfurization ability of the coated material, which was around 98% and 52% for 1 h and 5 h, respectively. It could be stated that the nickel site was more sensitive to sulfur phase as compared to CH₄. Furthermore, both reforming and desulfurization efficiencies tended to decrease during the process, ascribed to the fact that the hydrogen sulfur primarily chemisorbed on the metal phase of the surface, resulting formation of product layer with time. This layer was responsible for the inhibition effect on the diffusion of methane and hydrogen sulfur towards the active particles located inside the disc structure, expecting a decreasing trend for hydrocarbon degradation and sulfur adsorption. Therefore, it could be concluded that the limited behavior of methane

reforming in simulated gasification atmosphere resulted from the accumulation of sulfur on the disc surface and stronger interaction for Ni-S as compared to Ni-CH₄.

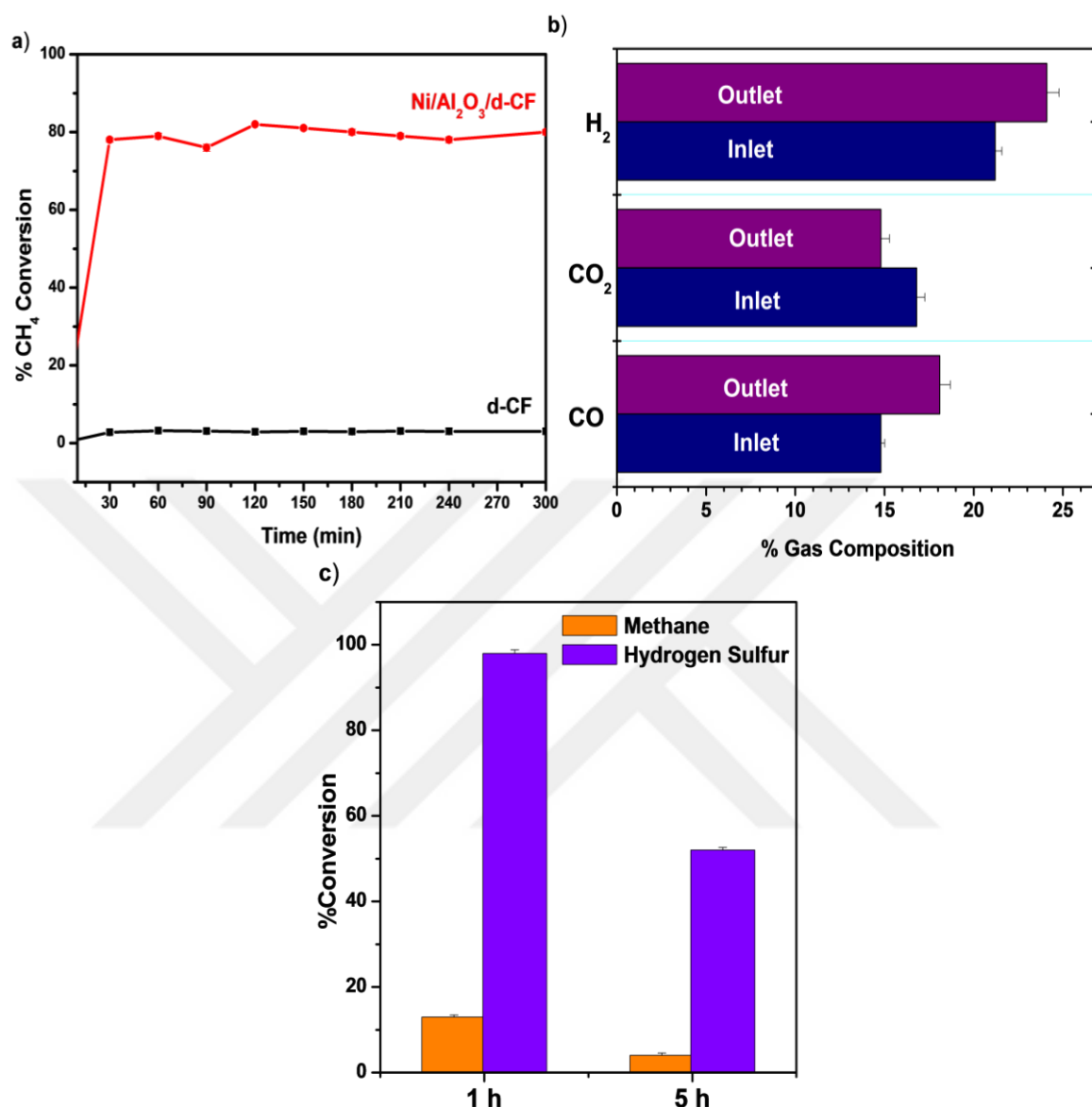


Figure 5.24: Reforming efficiency (a), changes in gas components (b), and the activity under H₂S flow (c)

Furthermore, the activity studies were performed to examine the performance of Ni/Al₂O₃/d-CF on tar elimination in the presence and absence of hydrogen sulfur. According to tar protocol CN/TS 15439, benzene could be presented as a tar compound; thus, benzene was utilized as a model component in this study [190]. The time-dependent catalytic performances with respect to methane and benzene conversion for two atmospheres were depicted in Figure 5.25. In sulfur-free environment, the degradation efficiency was found to be 73% and 85% for methane and benzene, respectively within 1 h and these values maintained at similar level at the

end of 5 h (Figure 5.25a). It was stated that Ni/Al₂O₃/d-CF could be also utilized to degrade cyclic hydrocarbon without loss of activity. In terms of sulfur-included environment, the conversion was reduced to approximately 5% and 60% for methane and benzene, respectively, after 5 h (Figure 5.25b). The deactivation trends in the presence of sulfur compounds were mainly due to the formation of nickel sulfide compounds. Interestingly, the reduction rate was less in benzene conversion as compared to methane reforming. This could be due to the fact that sulfur replaced with oxygen at the catalyst surface, then the free-oxygen provided the oxidation of the tar substrate, resulting less blocked benzene degradation. This result approved the promoting effect of H₂S on the degradation of benzene. Similar phenomena were observed in literature [191, 192].

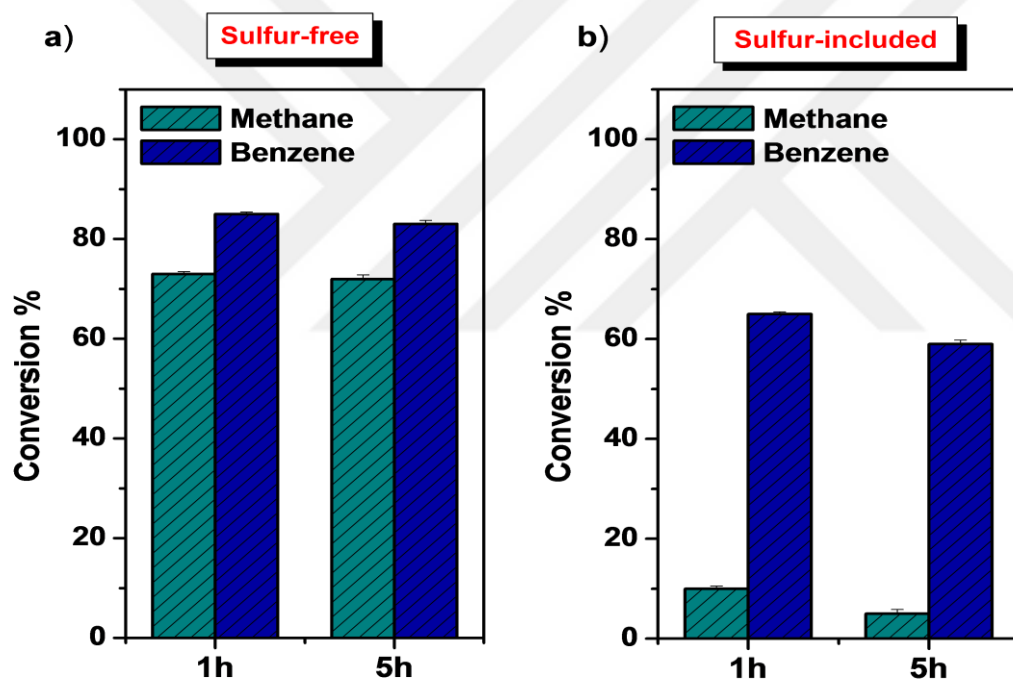


Figure 5.25: Reforming efficiencies under H₂S-free (a) and H₂S flows (b)

In addition, pressure-drop measurement was applied to analyze the filtration efficiency of Ni/Al₂O₃/d-CF, which was attributed to its ability on gas permeation during reforming process. The relevant results for fresh and spent catalytic structures were presented in Table 5.4. The un-utilized catalytic filter material gave pressure drop values of below 25 mbar under flowing the components of synthesis gas with and without hydrogen sulfur, indicating that the coated sample could provide sustainable filtration into gasifier [189]. Moreover, the fresh coated sample showed higher

pressure drop values as compared to the noncatalytic candle filter, resulting that the coated metal oxide phases decreased the pore volume of the filter sample. In case of the as-used ceramic, the higher rate of pressure drop increase was observed. This could be explained by considering that the possible accumulation of carbonaceous and sulfur components occurred during steam reforming.

Table 5.4: Pressure drop measurements under different atmospheres

Sample Type	Pressure Drop (mbar)			
	Fresh		Spent	
	<i>Sim. Gas. Atm.*</i>	<i>Sim. Gas. Atm.**</i>	<i>Sim. Gas. Atm.*</i>	<i>Sim. Gas. Atm.**</i>
d-CF	3.6	3.7	-	-
Ni/Al₂O₃/d-CF	10.2	10.5	11.2	11.5
20% CuZT/p-CF) + Ni/Al₂O₃/d-CF	14.2	14.5	18.7	18.9

*: The measurement was performed under simulated gasification atmosphere.

**: The measurement was performed under simulated gasification atmosphere including H₂S

5.3.4 Integrated System for Both Reforming and H₂S Adsorption

The activities of integrated filter system were evaluated for both hydrocarbon reforming and hydrogen sulfur adsorption under sulfur-free and sulfur laden gasification atmospheres. The removal efficiencies against time were depicted in Figure 5.26. As observed in Figure 5.26a, it was found that the degradation rate of methane (~62%) and benzene (~80%) almost had no fluctuation in the absence of H₂S during the 5h experiment. The statement supported that two active filter systems showed sufficient hydrocarbon cracking activities. However, the efficiencies were found in lower values than that of bare Ni/Al₂O₃/d-CF. It might be attributed to calcium silicate which leads to methanation, causing a decreased catalytic activity for hydrocarbon degradation. Noteworthy, the integrated process exhibited superior reforming efficiencies for methane and tar degradation in the presence of sulfur during the process time, which were 10 times higher for methane and 1.15 times higher for benzene than that of the single filter system (Figure 5.26b).

In same way, the H₂S adsorption capacity displayed efficient behavior as 96% removal during 1 h, then 71% removal was obtained after 5 h.

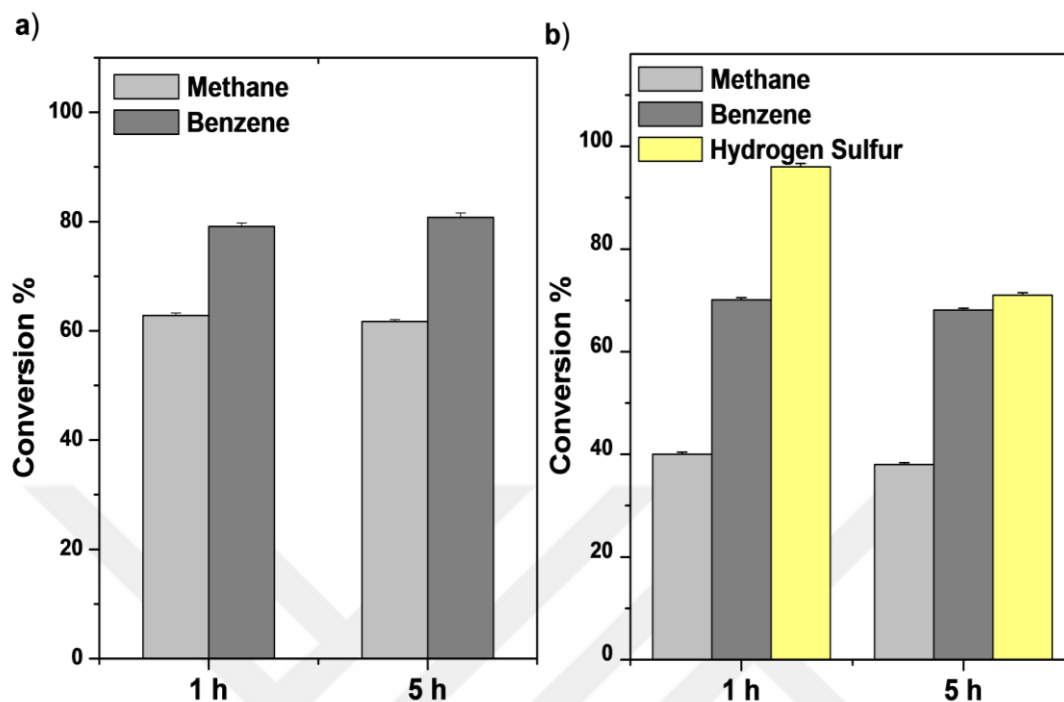


Figure 5.26: Reforming efficiencies under H₂S-free (a) and H₂S flows (b) in integrated system

Elemental mapping was performed for the spent filters in single-stage and two-stage removal processes to define nickel distribution and carbon formation. Figure 5.27 illustrates that the relatively more carbon deposition was observed in case of Ni/Al₂O₃/d-CF. This could be due to the fact that when metal active species occupied with sulfur in the progress of the reforming, hydrocarbon adsorption started to occur on support surface sites where it underwent acid site cracking, indicating that the cracking improved carbon deposition on the surface [193]. It could be suggested that higher interaction between nickel sites and sulfur caused larger carbon accumulation on the filter surface, lowering the reforming rate. In case of the integrated system (Figure 4.29b), lower carbon formation was observed, resulting higher methane and benzene degradation efficiencies. In addition, the distribution of Ni particles aligned well with its utilization rate during hydrocarbon cracking, resulting well-distribution was observed in the two-stage process. The pattern suggested that primary active layer acted as a protector site to take up sulfur for Ni phases, which achieved more activity for steam reforming in the integrated system. In addition, the pressure drop of the two-stages process was found to be 14.5 mbar before experiment and 18.9 mbar after

experiment, suggesting that the integrated catalytic system could provide sustainable filtration efficiency, as seen in Table 5.4. It could be therefore stated that the gradual removal process based on two- layer catalytic filter system would provide a new perspective for one-stage biomass gasification processes.

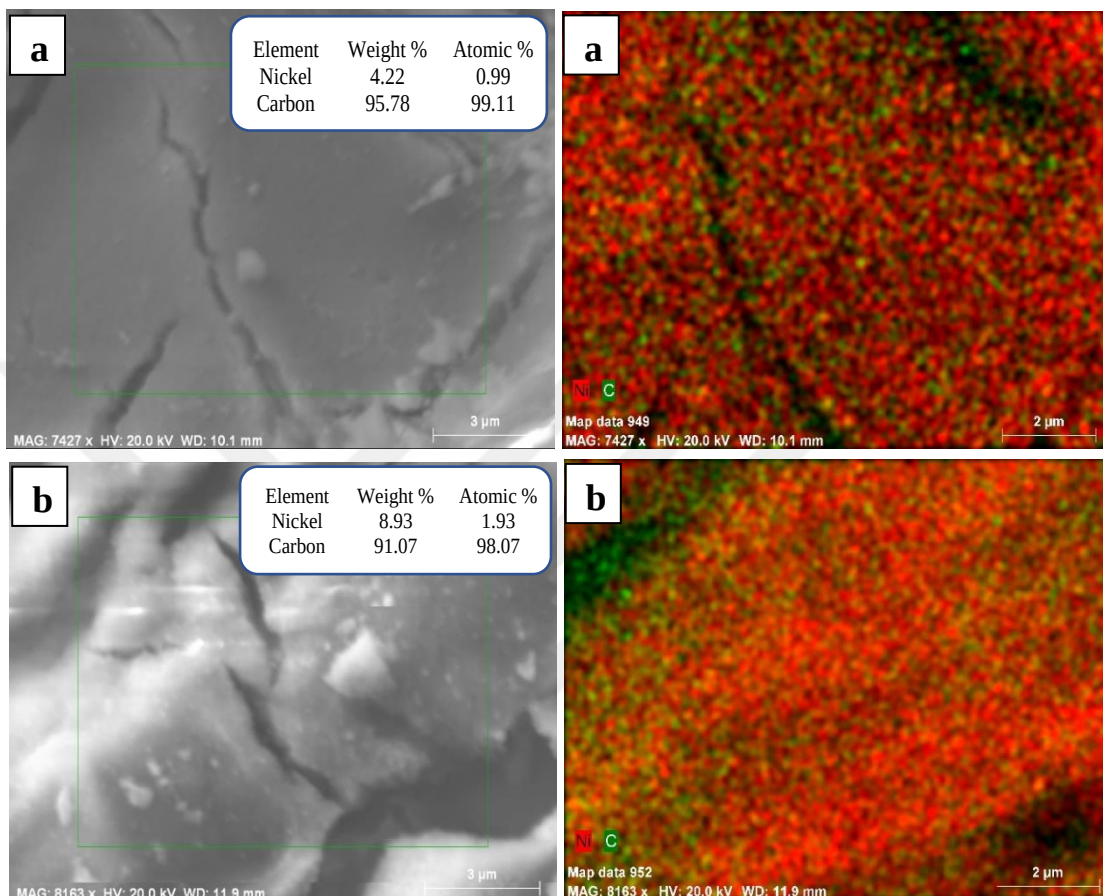


Figure 5.27: Elemental mapping of spent filters in one-stage (a) and integrated systems (b)

5.3.4.1 Effect of H₂S concentration

The experimental part demonstrated the fate of H₂S at three different concentrations of 50, 100 and 200 ppmv in methane and benzene degradations over the filter in integrated steam gasification tests. As depicted in Figure 5.28, the reforming efficiencies decreased at each H₂S concentration and the decrease of the hydrocarbon conversion rates was greater with increasing the sulfur amount. After 5h. the methane conversion were calculated as 51%, 47% and 38% in the presence of 50, 100 and 200 ppmv, respectively (Figure 5.28a). Meanwhile, the decreasing trend in the benzene degradation was observed as 75%, 72% and 69% during the increase of H₂S

concentration (Figure 5.28b). The reason of the inhibiting effect could be due to fact that the sulfur preferentially adsorbed the on active-metal sites as compared to hydrocarbon, lower catalytic activity. Furthermore, the inhibition effect on the rates was observed within 1h, and then it maintained at stable, indicating that the sulfur compound presence could actively participate at the fast formation of product layer on catalytic surface. In addition, the integrated system still showed high activity for benzene removal even if the presence of 200 ppm H_2S , suggesting that, the process could be presented as a promising sulfur-resilient catalytic system for high-qualified synthesis gas production via biomass gasification.

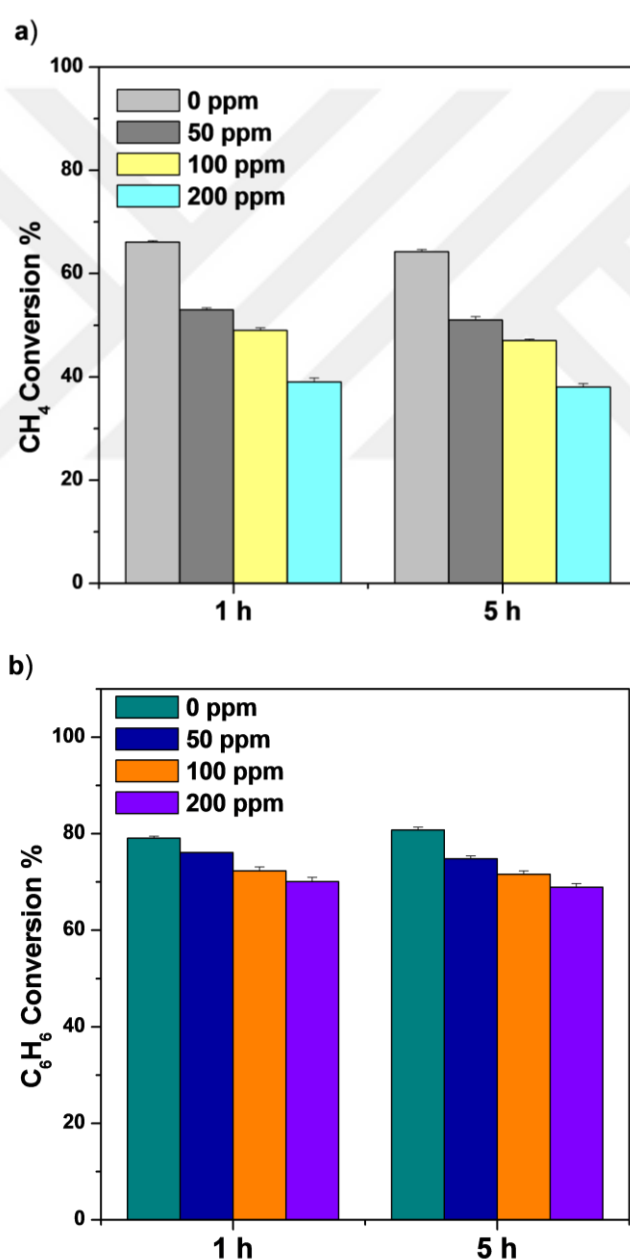


Figure 5.28 : Reforming rates under different H_2S concentrations

6. CONCLUSION

This thesis aimed to produce high-qualified synthesis gas by removing hydrogen sulfur during hydrocarbon degradation. For this, series of H₂S adsorbents were developed followed by combination with ceramic filter. The main remarks were summarized below in order:

- Commercial Zn₂TiO₄ was first utilized as a model adsorbent to determine the diffusion limitations driven by fluid velocity and temperature during desulfurization. The H₂S conversion was not affected by fluid rate, indicating that the external mass transfer limitation was not significant while the reaction rate was facilitated with temperature by decreasing Kirkendall effect. This statement was observed with TEM and EDS results: larger particles appeared on the spent samples at low temperature (450 °C) in which sulfur was highly accumulated on the adsorbent surface.
- The effect of the temperature on the rate of desulfurization was also examined by considering the change in the deactivation constant. The related values were found to be in same range, demonstrating that the desulfurization was kinetically controlled with a lesser degree of diffusion resistance through the product layer formation.
- The influence of reaction atmosphere on the desulfurization rate of commercial Zn₂TiO₄ was studied. The addition of hydrogen as reducing gas resulted in a decrease of the H₂S removal efficiency. This was due to the decrease active sites into the metal oxide lattice and this result was observed with XRD results which demonstrated the loss of the zinc titanate peaks. On the other hand, the related decreasing trend in gasification atmosphere was more prominent than that of H₂-environment because of the higher reduction degree.
- Secondly, the effect of copper doping into the zinc titanate structure was examined to obtain more effective H₂S removal performance under gasification atmosphere. In this sense, Cu-doped zinc titanates were synthesized by co-precipitation method. The XRD analysis showed the presence of hexagonal and cubic ZnTiO₃ phases and cubic Zn₂TiO₄. Besides, the XPS measurements confirmed the incorporation of copper ions into the zinc-based host lattice, resulting the formation of new inverse spinel structure (Cu_xZn_{2-x}TiO₄).

- The influence of Cu-content on the desulfurization was explored under gasification atmosphere. The addition of Cu in zinc titanate structure greatly increased the removal rate and 40% more H₂S adsorption was achieved when compared with non-doped zinc titanate. Based on XPS results, the incorporation of the copper decreased the required energy for the reaction, resulting higher oxygen concentration. Meanwhile, the copper addition provided formation of macro-porous structure, indicating the absence of external mass transfer limitation. On the other side, the metal-doping improved the resistance towards the reduction which was supported with XRD analysis. The peak intensities of zinc titanates were found to be higher in Cu-ZT samples as compared to bare ZT.
- During the desulfurization of Cu-ZT adsorbents, the reverse water-shift reaction was promoted and as a result of the reaction the water vapor was produced which had a detrimental influence on the H₂S adsorption.
- In the third part, the H₂S removal was further improved by developing an integrated gasification approach. For this, Cu-Zn₂TiO₄ incorporated with CaSiO₃ filters (CuZT/pCF) were constructed by ball-milling technique and the successful incorporation was verified from XRD and FTIR characterization methods. Considering the SEM images, the ball-milling method did not destroy the fiber structure of CaSiO₃ and the zinc-based particles were attached on the filter with high distribution ratio.
- The CuZT/p-CF composite adsorbents disclosed higher sulfur removal performance due to the enhanced active sites and diffusion rate. Furthermore, 20%CuZT loading remarkably enhanced the sulfur resistance under reducing and oxidizing atmospheres by increasing affinity and preventing diffusion limitation.
- Moreover, an active filter material including Ni/Al₂O₃ (Ni/Al₂O₃/d-CF) was prepared by impregnation method in order to further utilize as a cracking catalyst in the integrated system. The existence of nickel and alumina in the filter structure was confirmed by XRD data. The Ni/Al₂O₃/d-CF exhibited higher catalytic activity towards methane and benzene steam reforming in H₂S-free synthesis atmosphere. The pressure-drop measurement revealed the appropriate usage of Ni/Al₂O₃/d-CF sample in continuous biomass gasification.

- In H₂S-environment, the methane and benzene degradation in the single stage over Ni/Al₂O₃/d-CF catalyst dramatically decreased due to nickel poisoning with sulfur. As compared to the methane conversion, the benzene reduction ratio was lower which was ascribed to the replacement of oxygen with sulfur promoting benzene oxidation.
- The hindered performance of Ni/Al₂O₃/d-CF was accomplished by integrating with the catalyst filter with the 20%CuZT/pCF adsorbent in the two-stage removal process. The integrated process displayed superior reforming efficiencies for methane and benzene degradation in the H₂S atmosphere, which were 10 times higher for methane and 1.15 times higher for benzene than that of the single stage system. Meanwhile, the desulfurization rate of 71% was achieved at the end of 5 hours. The results confirmed the effectiveness of the integrated system for hydrocarbon cracking in the presence of H₂S.
- The elemental mapping was conducted to explore the carbon and nickel distribution over the spent filters. When compared the single-stage with the integrated system, the accumulation of the carbon on the catalyst surface was found higher, resulting decreased conversion. On the other side, in the integrated system the nickel was well distributed on the filter surface due to less blockage of the active centers with sulfur.

In overall, this thesis contemplated possible improvement of zinc titanate using copper as a dopant that provides an appropriate adsorbent for effective desulfurization implementation under biomass gasification atmosphere. The research was also envisioned that the incorporation of the materials with ceramic filter promoted to obtain high desulfurization efficiency. Furthermore, the adsorptive system would offer protective layer for catalytic filter structure utilized in a gasifier. Therefore, this study opens new insights in utilizing an integration process which combined desulfurization and tar reforming stages for advanced biomass gasification process.

INFORMATION OF THE SUPPORTING INSTITUTION

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Publication and Patent List:

- [1] Ö. Tuna, A. Bal, G. Güçlü, Investigation of the effect of hydrolysis products of postconsumer polyethylene terephthalate bottles on the properties of alkyd resins, Polym. Eng. Sci. 53(2013), 176-182.
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