

Article

Evaluating the Impact of Preparation Method on the Performance of Metal-Oxide Adsorbents/Catalysts for Ethyl Mercaptan Removal from Natural Gas

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Abstract

The presence of toxic, corrosive, and environmentally harmful sulfur compounds within natural gas streams necessitates their removal to ensure compliance with fuel quality standards and regulations. Previous studies into MMOs (mixed metal-oxides) as adsorbents or catalysts for sulfur compound removal have generally focused on hydrogen sulfide (H₂S); however, few studies have assessed the removal of organic sulfur compounds such as ethyl mercaptans. The purpose of this research is to investigate the effects of various preparation routes on the performance of supported metal-oxide catalysts that remove ethyl mercaptans from natural gas; specifically, filtration-based and evaporation-based catalyst synthesis methods were investigated. A set of different catalysts—Mn, Cu, Zn, Ni, and a composite (Mn-Cu-Zn-Ni)—were prepared using filtration or evaporation solvent removal in this research and characterized by BET, FTIR, XRD, SEM, EDS, and XPS, and their sulfur-removal performance was evaluated through fixed-bed breakthrough experiments under representative operating conditions (25 °C, 200 psi, 36 mL/min). The results demonstrate that catalysts prepared via evaporation consistently exhibit greater sulfur adsorption performance compared to catalysts prepared through filtration, which is consistent with improved surface oxide exposure. Structural characterization further showed that evaporation-assisted preparation promoted improved surface oxide development, greater surface heterogeneity, and more accessible surface morphologies. Among the investigated catalysts, evaporation-prepared Mn and Cu catalysts achieved the highest breakthrough times of approximately 1410 min and 1350 min, respectively, exceeding the commercial benchmark catalyst (1200 min) under identical operating conditions. These findings demonstrate that the evaporation method enables more effective utilization of surface metal-oxide active sites involved in sulfur adsorption and surface redox interactions. Overall, this work establishes evaporation as a superior and scalable preparation strategy for metal oxide catalysts and provides important structure-performance insights for the design of cost-effective catalysts for industrial natural gas desulfurization, particularly for the removal of organic sulfur compounds such as ethyl mercaptan from natural gas.

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1. Introduction

Sulfur compounds in natural gas streams represent problems of toxicity, corrosion, odor, and harm to equipment downstream. Sulfur compounds could also act as poisons for catalysts used for the direct or indirect conversion of methane into fuels and chemicals. The removal of sulfur compounds is required by specifications on fuel quality, process safety, and environmental regulations. Mercaptans are particularly troublesome among sulfur-containing species as their selective removal from a feedstock can be difficult, and they may still be present in amounts that exceed specified limits even after reduction in other sulfur species to acceptably low levels. In particular, organic sulfur compounds are of interest due to their presence in gas systems and the high degree of affinity these species exhibit, with active surface sites making them an ideal model compound for studying adsorbent or catalyst activity toward natural gas treatment [1–3].

Metal oxides (MOs) are being researched as potential catalysts or adsorbent materials for removing sulfur from gas streams. They present various advantages over other adsorbing materials, including a large number of active redox and adsorptive sites on the surface, and they may also have variable compositions at lower costs than many adsorbing materials. Many transition metal oxides such as those containing Mn, Cu, Zn, or Ni have been studied for sulfur capture based upon the interactions that occur between these oxides and sulfur-based molecules. Most studies conducted using MOs for sulfur removal have focused on H₂S removal rather than organic sulfur compounds, which are important when considering the use of MMOs in industrial gas treatment processes [4,5].

Sulfur removal efficiency in a metal oxide–support system depends upon how well the active phase of the metal is stabilized and dispersed on the surface of the support. Because of this dependence, the method used to prepare the catalyst can be just as or even more important than the composition of the catalyst. The preparation method strongly influences the surface characteristics of supported metal oxides, including precursor deposition, metal–support interactions, and the availability of surface oxide sites that govern sulfur-removal performance. Of the many different synthesis techniques that have been developed for supported catalysts, impregnation routes are among the simplest and most cost-effective methods available to researchers and industry personnel for preparing catalysts due to their versatility [6–8].

The process of removing solvents during catalyst preparation is an essential and commonly overlooked part of the overall preparation process. During the solvent removal stage, there are many factors to consider such as the redistribution of dissolved precursors within a support by virtue of capillary flow, diffusion, adsorption–desorption, and/or local supersaturation effects. These factors can greatly affect if a synthesized catalyst will exhibit uniformly dispersed active oxides or suffer from metal loss, poor dispersion, or uneven surface coverage. The most commonly used method for solvent removal is filtration. Filtration involves separating the solid from the liquid phase prior to completing solvent removal [7–10]. Although drying and precursor redistribution are recognized as important steps during catalyst preparation, relatively few studies have systematically evaluated how solvent removal routes influence the structural and surface properties of halloysite-supported metal-oxide systems for ethyl mercaptan removal. Most previous investigations have focused primarily on catalyst composition, promoters, or adsorption performance rather than on the influence of solvent removal during synthesis [11–20].

The research in this study utilized a series of supported metal oxides formed over a halloysite support by two solvent removal methods: filtration and evaporation. These removal methods are utilized to compare the effects of both solvent removal methods on the adsorption of sulfur compounds from natural gas. Halloysite is an attractive candidate as a support due to its aluminosilicate structure with a high density of surface hydroxyl groups and ability to deposit metal oxides. Four single-metal catalysts of Mn, Cu, Zn, and Ni, along with one composite (Mn-Cu-Zn-Ni), were produced and analyzed via BET, FTIR, XRD, SEM, EDS, and XPS. Following characterization of each catalyst, their sulfur adsorption performance was evaluated using a fixed-bed reactor at representative process conditions (25 °C, 200 psi, 36 mL/min) [10–18].

This research aims to evaluate the effects of filtration and evaporation preparation routes on the sulfur-removal performance of halloysite-supported metal-oxide adsorbents/catalysts. Particular emphasis is placed on how these preparation methods influence surface oxide development, metal–support interactions, surface chemical characteristics, and sulfur-removal efficiency [8,13]. This study establishes relationships between solvent removal method, catalyst structure, surface properties, and sulfur-removal performance while evaluating the feasibility of evaporation as a simple and scalable preparation route for halloysite-supported metal-oxide adsorbents/catalysts.

2. Results and Discussion

2.1. Analysis of Surface Morphology of the Prepared Catalyst

2.1.1. Analysis of BET Data of Filtration vs. Evaporation-Prepared Catalysts

The BET textural characteristics of the single-metal and composite catalysts synthesized using evaporation and filtration as shown in Table 1 demonstrate that the method used to remove solvents has a significant effect on the ultimate structure of the catalysts, including their surface area, pore volume, and pore size. These textural characteristics strongly influence sulfur adsorption behavior by affecting surface accessibility and diffusion pathways within the catalyst structure [18,19].

Table 1. Textural properties of catalysts prepared via filtration and evaporation methods.

Catalyst	Filtration Method			Evaporation Method		
	Surface Area m ² /g	Pore Vol- ume cm ³ /g	Pore Size nm	Surface Area m ² /g	Pore Vol- ume cm ³ /g	Pore Size nm
Manganese	10.833	0.091	27.860	43.308	0.223	17.300
Copper	9.651	0.076	26.750	18.292	0.125	23.910
Zinc	38.769	0.213	18.790	14.034	0.096	27.480
Nickel	40.218	0.201	16.550	23.405	0.118	22.240
Composite	21.783	0.096	17.200	17.717	0.133	24.180

A clear pattern exists for both the manganese and copper samples prepared using the two methods of preparation: the evaporated samples had significantly larger surface areas and pore volumes than those that were prepared via filtration. The surface area of Mn was doubled: it went from a surface area of 10.833 m²/g to 43.308 m²/g. The pore volume also increased: it went from a pore volume of 0.091 cm³/g to a pore volume of 0.223 cm³/g. Similar increases occurred in the surface area and pore volume of Cu. The surface area increased by nearly double, from 9.651 m²/g to 18.292 m²/g, and the pore volume increased by almost a factor of 2 from 0.076 cm³/g to 0.125 cm³/g. These findings suggest that the slowest rate of solvent loss occurs when solvents are removed by evaporation, which allows for a more developed network of pores and improved accessibility of the interior

surface. The observed differences suggest that the solvent removal route influenced the final distribution of the deposited oxide phases within the halloysite support [7,9,20].

In contrast, zinc and nickel catalysts showed an inverse relationship to the method of preparation; the filtration method resulted in higher surface areas and pore volumes compared to the evaporation method. Both the surface area and pore volume of Zn were reduced significantly upon use of the evaporation method. The surface area of Zn decreased by approximately 64% (from 38.769 m²/g to 14.034 m²/g) and the surface area of Ni decreased by approximately 42% (from 40.218 m²/g to 23.405 m²/g) due to use of the evaporation method. The same was true for the pore volume measurements. These results indicate that the effect of the method of preparation can be dependent on the specific metal and its interaction with the support material during precipitation and solidification. The lower BET surface area and pore volume observed for some evaporation-prepared samples suggest that the solvent removal route influenced the final distribution and accessibility of the deposited metal-oxide phases within the halloysite support. However, the exact physicochemical interactions occurring during solvent removal require further investigation. The differences in BET properties between filtration and evaporation samples indicate that the preparation route influenced the accessibility of the surface oxide environments [6,21].

The average pore sizes presented in this paper also show how the structure of each material changed after evaporation. Evaporation produced a reduction in pore size for Cu, as evidenced by the slight measured reduction from 26.750 nm to 23.910 nm. Zn, Ni, and the composite material showed increases in pore size, with a significant increase from 18.790 nm to 27.480 nm for Zn; an even greater increase from 16.550 nm to 22.240 nm for Ni; and a moderate increase from 17.200 nm to 24.180 nm for the composite material. Except for Cu, the pore size results indicate that the preferred result of evaporation was the generation of larger and thus more easily accessed mesopores (2–50 nm pores that enhance adsorbate diffusion and active-site accessibility). Even the Cu pores formed by evaporation are comparable to Zn, Ni, and the composite material. Larger and thus more easily accessed mesopores are beneficial for gas phase adsorption as they provide less resistance to diffusion for sulfur-containing molecules through the pore space toward available active sites on the surface. Mn did not follow this pattern since its pore size actually decreased from 27.860 nm to 17.300 nm, with both surface area and pore volume showing significant increases. Thus, evaporation in the Mn catalyst appears to promote the formation of smaller mesopores (2–50 nm) rather than fewer larger pores, leading to improved surface accessibility as a result of the reduced average pore diameter. The observed pore-size variations suggest differences in oxide distribution and surface accessibility between the preparation methods [19,22,23].

For the Mn-Cu-Zn-Ni composite catalyst, with respect to surface area, there was a modest decrease (21.783 m²/g vs. 17.717 m²/g) during transition from filtration to evaporation. Conversely, both the pore volume and pore diameters increased by 39% (0.096 cm³/g vs. 0.133 cm³/g) and 40% (17.200 nm vs. 24.180 nm), respectively. While the total surface area of the composite prepared through evaporation was marginally less, the increase in pore volume and pore diameter clearly indicates that the pores were more open and accessible than those produced using filtration. The greater porosity can lead to better breakthrough behavior than a minor increase in BET surface area alone since access to pores as well as diffusional resistance can dominate the use of available sites in adsorption/catalytic reactions involving gases [18,21,22]. Hence, the improvement in breakthrough behavior exhibited by the Mn-Cu-Zn-Ni composite prepared via evaporation is also reflected in an enhanced pore structure.

These differences are consistent with the SEM, EDS, and XPS results, which collectively indicate greater surface exposure and accessibility of the active oxide phases for the

evaporation-prepared materials. Overall, the BET data show that evaporation does not simply increase or decrease all textural parameters uniformly but instead alters the catalyst structure in a way that depends on the metal precursor system and its interaction with the support during drying. In general, evaporation tends to favor larger pore accessibility and better pore connectivity, while filtration generally produced comparatively less structurally heterogeneous surface morphologies.

2.1.2. XRD Analysis of Catalysts Prepared by Filtration vs. Evaporation

XRD patterns for the pristine halloysite support and the prepared catalysts are shown in Figure 1. Using diffraction techniques, we evaluated the effect of the process by which the solvents were removed from the solution (evaporation or filtration) on the crystalline phases formed, the crystallinity of the oxide phases, and the crystallite development of the metal oxides that were deposited onto the surface of the halloysite support. Sharp and intense diffraction peaks generally indicate larger and more crystalline oxide domains, whereas broader peaks are commonly associated with smaller crystallite sizes and stronger metal–support interactions. The halloysite support (001) reflection at approximately 12° and an amorphous aluminosilicate region at 18–25° were seen in both the pristine support and all the supported catalysts; this demonstrates that there was no structural damage to the halloysite during catalyst synthesis [6,21].

Mn catalysts (for filtration and evaporation) showed MnOx-related reflections near 29°, 36°, 44°, 50°, and 60°, assigned mainly to Mn₃O₄/Mn₂O₃ phases (ICDD PDF: 24-0734 and 41-1442). The evaporation-prepared Mn sample showed broader and less intense MnOx reflections than the filtration-prepared sample, suggesting smaller crystallite domains. Cu catalysts (for filtration and evaporation) showed CuO reflections near 32.5°, 38.7°, and 58.3° (ICDD PDF: 48-1548), with weak features near 42–43° attributed to Cu₂O (ICDD PDF: 05-0667). The evaporation-prepared Cu sample exhibited sharper CuO-related peaks, indicating better crystalline oxide development. Zn catalysts showed ZnO reflections at 31.7°, 34.4°, 36.2°, 47.5°, 56.6°, and 62.8° (ICDD PDF: 36-1451), while Ni catalysts showed NiO reflections at 37.2°, 43.3°, and 62.9° (ICDD PDF: 47-1049). The composite catalysts showed overlapping reflections that were associated with ZnO, CuO/Cu₂O, NiO, and MnOx phases; therefore, it was confirmed that a combination of different metal oxides was successfully introduced into the catalyst system. Although both preparation methods produced similar mixed metal-oxide phases, the improved peak definition and reduced peak broadening observed for the evaporation-prepared composite catalyst suggest differences in crystallite development and oxide phase evolution compared with the filtration-prepared catalysts.

Overall, the XRD patterns demonstrate that the solvent removal method significantly influenced oxide phase development and crystallinity, with the magnitude of these effects depending on the deposited metal species. The evaporation method promoted better crystallization of the ZnO and CuO phases, whereas the broader MnOx and NiO reflections suggest the formation of smaller crystallite domains compared with the corresponding filtration-prepared catalysts.

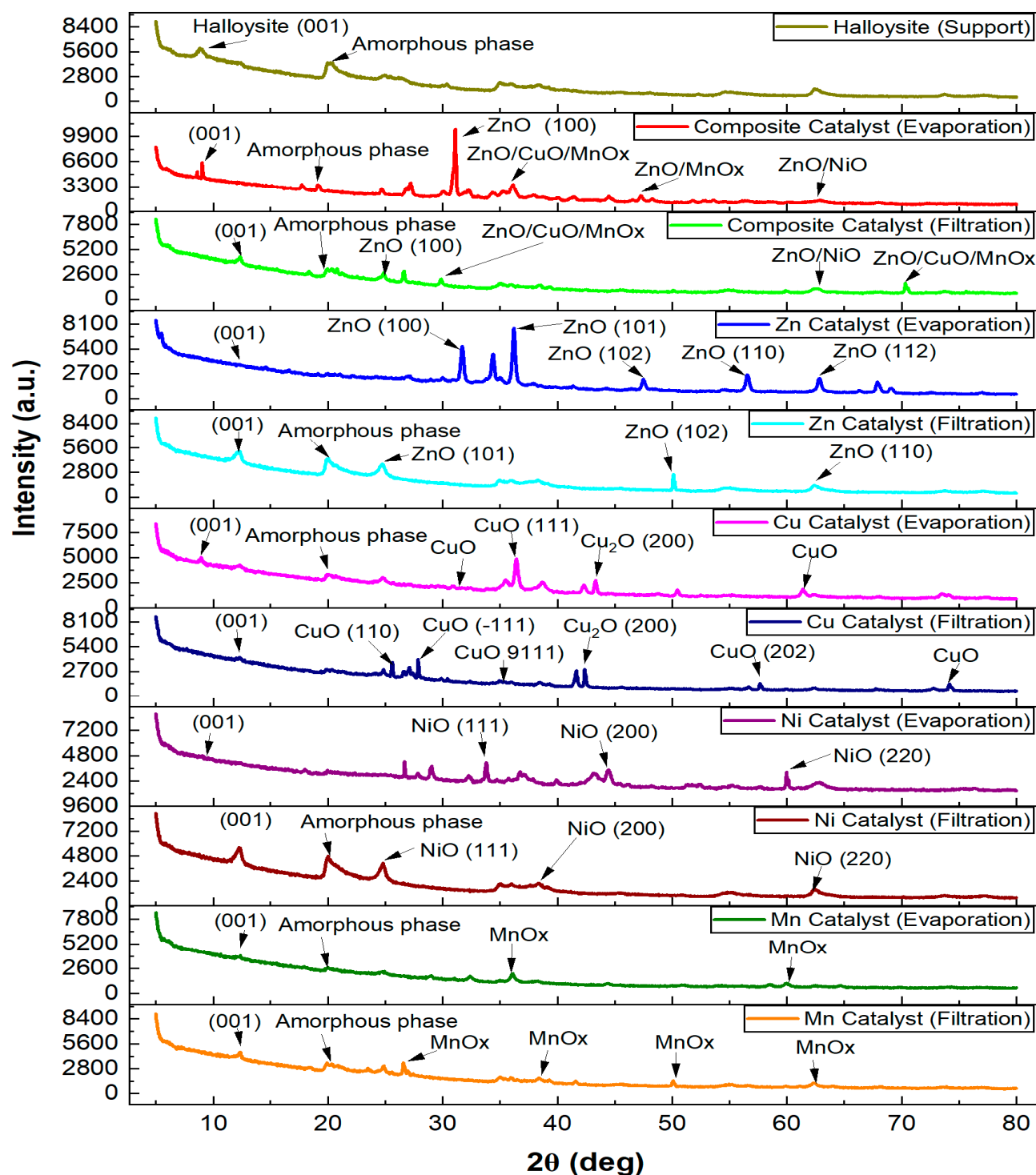


Figure 1. XRD pattern of the catalysts.

2.1.3. FTIR Analysis of Catalysts Prepared by Filtration vs. Evaporation

FTIR spectra of halloysites (support) and catalysts prepared using the filtration or evaporation methods are presented in Figure 2. The FTIR spectrum of pristine halloysite was included for direct comparison to distinguish support-related vibrations from changes associated with metal-oxide deposition. Also, characteristic bands representing the halloysite framework were found to remain present after preparation of the catalyst,

indicating that the aluminosilicate structure of the support was preserved. The bands observed within 3695–3620 cm^{-1} correspond to structural OH stretching vibrations associated with halloysite, while the broad region centered within 3450–3250 cm^{-1} is attributed to hydrogen-bonded hydroxyl groups and adsorbed water molecules [10,24]. The band near 1635–1620 cm^{-1} corresponds to H-O-H bending vibrations of adsorbed and interlayer water molecules [24,25]. In the fingerprint region, the strong band centered around 1035–1010 cm^{-1} is assigned to Si-O stretching vibrations of the aluminosilicate framework, whereas the band near 915–910 cm^{-1} corresponds to Al-O-H bending vibrations associated with halloysite [24–27]. Additional framework-related curves observed around 1100–1080 cm^{-1} and 790–750 cm^{-1} are associated with Si-O stretching modes and Si-O bending modes, respectively [24,26]. Compared to the filtration-prepared catalysts, the evaporation-prepared catalysts were characterized by a broader and more easily identifiable hydroxyl-related peak within 3450–3250 cm^{-1} , as well as a more distinct H-O-H bending band at 1635–1620 cm^{-1} . Additionally, the framework-related peaks found at approximately 1035–1010 cm^{-1} and 915–910 cm^{-1} were clearer and sharper for the evaporation-prepared catalysts. These characteristics are indicative of an increased degree of surface hydroxylation, enhanced interactions between the metal and support, and changes in the local surface chemical environment following evaporation-assisted synthesis [6,24,26].

The evaporation (Mn and Cu) catalysts exhibited the most noticeable changes in the hydroxyl and framework-related bands compared with their filtration-prepared counterparts. Specifically, the Mn and Cu catalysts demonstrated more pronounced bands at approximately 3420–3340 cm^{-1} , 1630 cm^{-1} , and 1030–1010 cm^{-1} . The evaporation-prepared Zn and Ni catalysts also showed broader hydroxyl-related bands and sharper framework-related bands at approximately 1030 cm^{-1} and 910–915 cm^{-1} [24–29]. The composite catalyst that was prepared by evaporation had broader bands related to hydroxylated groups in the range 3450–3300 cm^{-1} ; a much better-defined H-O-H bending band at approximately 1630 cm^{-1} ; and more intense bands associated with the silicate framework at about 1030 cm^{-1} as well as in the range of 910–915 cm^{-1} compared to the composite catalyst prepared by filtration. In addition, the composite catalyst prepared by evaporation contained additional vibrational features within the 1100–1080 cm^{-1} range that were more pronounced than those observed in the composite catalyst prepared by filtration.

Overall, the FTIR data indicate that the removal method greatly affected the chemical surface characteristics of the catalyst. Evaporation-assisted synthesis consistently resulted in more distinguishable vibrational features associated with hydroxyl groups and the halloysite framework, suggesting differences in the local chemical environment and metal-support interactions between the evaporation- and filtration-prepared catalysts. These observations are consistent with the complementary results obtained from XRD, EDS, and XPS analyses [6,24–29].

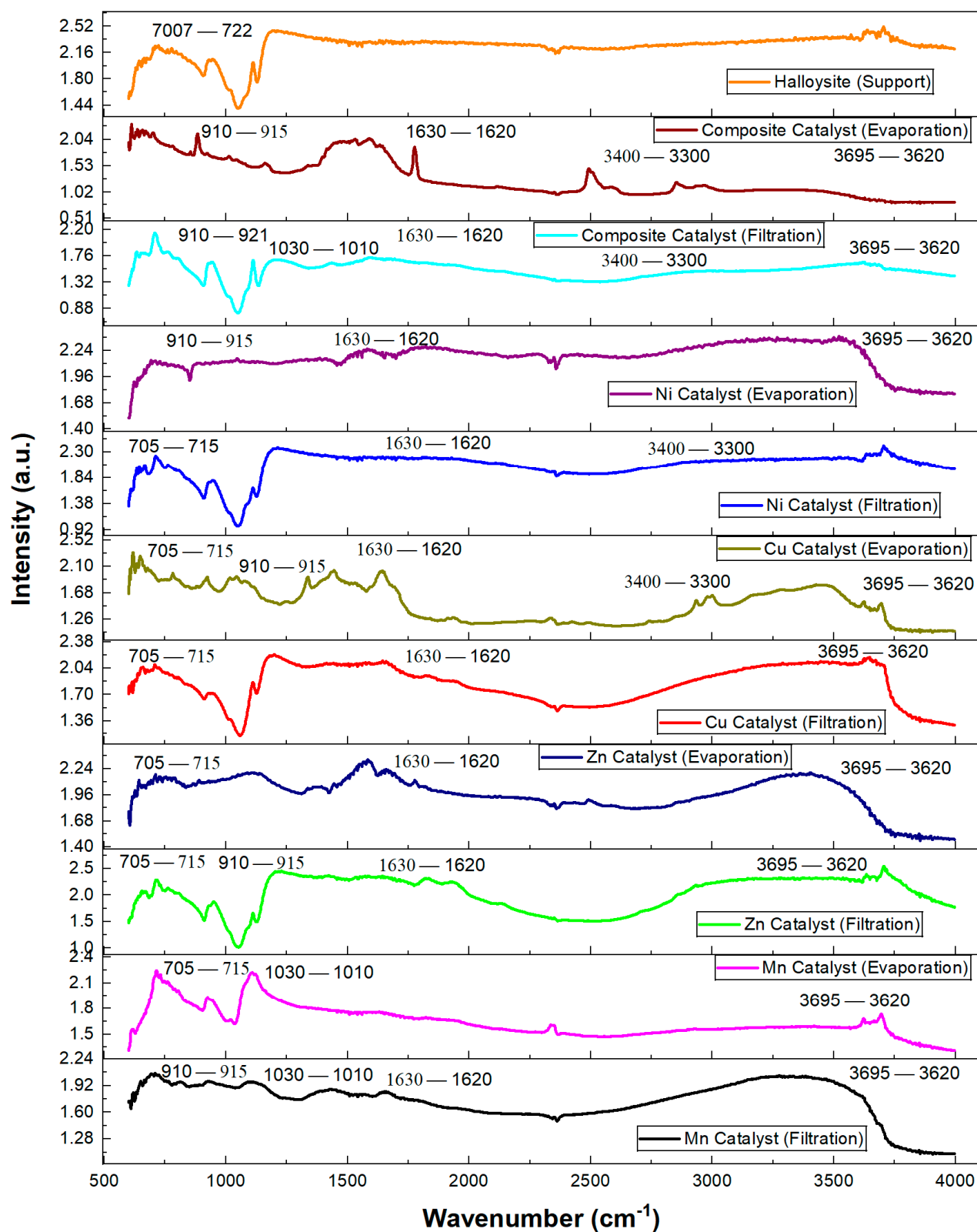


Figure 2. FTIR spectrum of the catalysts.

2.1.4. SEM Analysis of Catalysts Prepared by Filtration vs. Evaporation

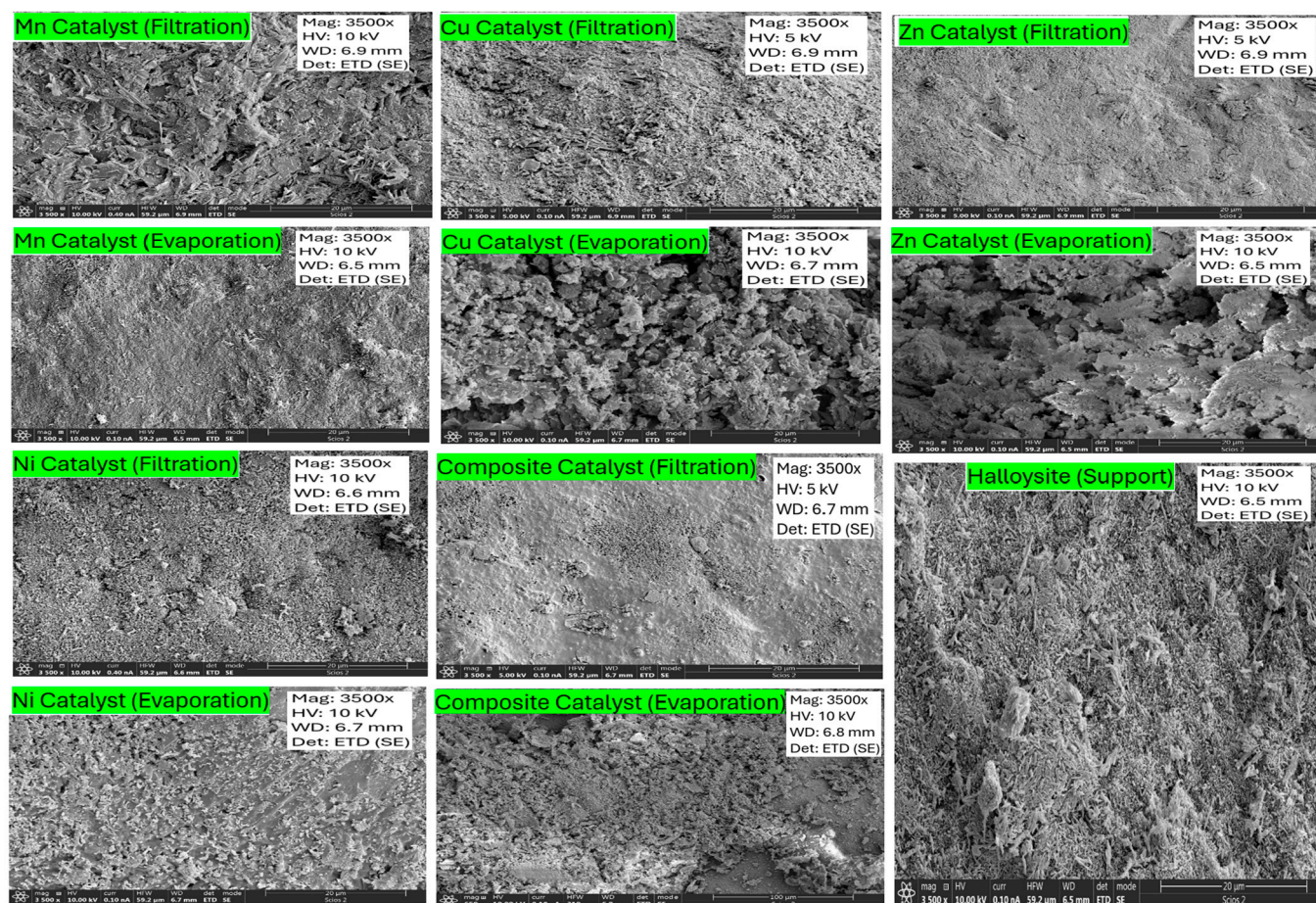
SEM images of the prepared catalysts are presented in Figure 3. The analysis was performed to compare the surface morphology and structural organization of catalysts prepared using filtration and evaporation solvent removal methods. Although all catalysts possessed identical chemical compositions, noticeable differences in surface texture, particle aggregation, and structural heterogeneity were observed depending on the preparation route. In general, the filtration-prepared catalysts exhibited relatively smooth, compact, and dense surface morphologies with limited structural irregularity, whereas the evaporation-prepared catalysts displayed rougher and more heterogeneous surface structures with increased particle fragmentation and agglomeration. Morphologically, these differences demonstrate that removal of the solvents had an enormous effect on how the metal oxides were structurally organized in the product [6,8,28,30,31].

In comparison to the Mn catalyst prepared by filtration, the Mn catalyst prepared by evaporation was seen as having a greater degree of surface fracturing and fragmentation. The overall structure was also less ordered than the Mn catalyst prepared using filtration. These findings suggest morphological changes that may be associated with differences in oxide deposition behavior between preparation methods [32,33]. Like the Mn catalyst, the Cu catalyst prepared via filtration demonstrated a more uniformly packed and smooth surface morphology. On the other hand, the Cu catalyst prepared via evaporation demonstrated a much rougher surface with larger agglomeration domains and more irregular surface features. These findings suggest altered surface structural organization following evaporation-assisted preparation and structural formation of Cu-containing oxide species after evaporation-assisted preparation [6,33]. The filtration-prepared Zn catalyst exhibited a relatively compact and uniform surface structure that was minimally affected by structural variations. In contrast, the Zn catalyst prepared using evaporation was much more uneven, heterogeneous, and had an increased number of loosely bonded aggregates with irregular structures compared to the filtration-prepared sample. SEM does not allow for direct confirmation of oxide dispersion nor quantitative determination of porosity; however, the increased heterogeneity associated with these samples suggests greater surface area development as well as greater retention of the metal oxides when prepared via evaporation [34,35,36].

The filtration-prepared Ni catalyst had a compact, relatively uniform surface with little structural variance. The evaporation-prepared nickel (Ni) catalyst had a less uniform, more fractured surface with increased surface roughness and particle aggregation. These characteristics indicate that there are strong structural interactions between the Ni oxide species deposited on the halloysite support after evaporation-assisted preparation [8,28].

The filtered composite catalyst looks relatively uniform, with a smooth surface morphology with less structural variability than the evaporated composite catalyst. The evaporated composite catalyst appeared rougher and showed a high degree of structural variability. The increased structural variability of the evaporated composite catalyst indicates that the mixed metal-oxide phases appeared more structurally integrated through slow removal of the solvent [33,34].

The overall SEM images illustrate that solvent removal significantly affects the morphology of the catalysts. The solvent removal process used to prepare each catalyst resulted in a consistently rougher and more structurally variable surface when using evaporation rather than filtration. Although SEM is unable to provide quantitative information regarding pore volume or dispersion of metals, the morphological differences seen in the SEM images are consistent with the BET, EDS, XRD, FTIR, and catalytic performance results that provide evidence on the enhanced development of the surface texture and retention of active metals for evaporation-prepared catalysts.



All images were acquired using a scanning electron microscope under the indicated settings.

Det: ETD SE (Everhart-Thornley Detector, Secondary Electrons); HV: Accelerating Voltage; WD: Working Distance; Curr: Beam Current; HFW: Horizontal Field Width

Figure 3. SEM images of the catalysts.

2.1.5. EDS Analysis of Catalysts Prepared by Filtration vs. Evaporation

EDS data proved the existence of both the anticipated support-derived and metal-derived species within the prepared catalysts and demonstrated that the method of preparation had a significant influence on both the amount of surface elemental retention as well as elemental accessibility, as shown in Table 2. The results confirmed the presence of halloysite elements (Al, Si, and O) together with the corresponding active metal species (Mn, Cu, Zn, and Ni) within the prepared catalysts. Sodium was also detected in some samples due to the use of NaOH during pH adjustment, which is consistent with previous reports for catalysts synthesized under alkaline conditions. As expected due to their composition, Al, Si, and O peaks were consistent across all of the samples as halloysite has been previously reported to have chemical distinctions between its outer surface layer rich in silica and inner surface layer rich in alumina [10,13,30–32]. The EDS results show a significant influence on the surface elemental composition of the active metals and how well they are retained in relation to the preparation method. Generally, the evaporation-prepared catalysts had substantially greater amounts of transition metals along with less relative contributions of Al and Si from the halloysite support than filtration-prepared catalysts. As such, the EDS data indicate greater near-surface representation of active metal-oxide species in the evaporation-prepared catalysts. However, direct accessibility of interfacial oxide sites was inferred only in combination with BET, SEM, XPS, and sulfur-removal performance results, rather than from EDS alone.

Table 2. Chemical composition of the six catalysts obtained by EDS analysis (Filtration/Evaporation: %Value).

Element	Halloysite (Support)		Mn Catalyst		Cu Catalyst		Zn Catalyst		Ni Catalyst		Composite Catalyst	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
Al	18.6	22.38	9.96/7.05	6.27/5.02	7.47/8.99	5.01/7.19	29.05/4.7	20.62/3.8	14.9/2.85	9.85/2.14	13.42/8.8	9.53/5.44
Si	17.59	21.48	14.68/5.5	8.87/3.81	8.19/7.81	5.28/6.00	14.73/4.5	10.05/3.5	14.83/2.8	9.41/2.05	15.67/-	10.69/-
Mn			1.84/27.6	0.57/9.67							2.64/2.55	0.92 / 0.77
Cu					16.05/25.46	4.57/8.64					3.97/2.18	1.20/0.57
Zn							1.77/37.6	0.52/12.6			2.78/3.38	0.81/0.86
Ni									3.53/21.4	1.07/7.40	2.33/-	0.76/-
C			21.28/24.18	30.1/38.7	24.88/12.14	37.47/21.80	9.1/16.29	14.52/29.69	14.33/11.19	21.28/18.88	13.04/30.32	20.82/42.07
O	63.81	56.14	48.36/35.58	51.33/42.77	39.33/33.15	44.47 / 44.69	45.35/36.82	54.29/50.36	52.4/39.3	58.38/49.87	46.15/38.01	55.27/39.58
Na			3.88/-	2.86/-	4.08/12.4	3.21 / 11.68			0.01/22.3	0.01/19.6		

The amount of Mn increased dramatically for the Mn catalyst; it went from 1.84 wt% and 0.57 at% in the filtration-processed sample to 27.62 wt% and 9.67 at% in the evaporation-processed sample. Simultaneously, there was a decrease in the relative Al content, from 9.96 wt% to 7.05 wt%, as well as a decrease in Si content from 14.68 wt% to 5.57 wt%. The significant increase in Mn along with a corresponding reduction in the relative contents of the support-related components (Al and Si) indicate that evaporation resulted in greater preservation of metal precursor species during synthesis and surface exposure of MnOx species relative to the filtration method. Similarly, Cu content also increased from 16.05 wt% and 4.57 at% in the filtration-processed catalysts to 25.46 wt% and 8.64 at% by evaporation. Moreover, the Al content increased somewhat (from 7.47 wt% to 8.99 wt%), but the Si content did not vary greatly (from 8.19 wt% to 7.81 wt%). Nonetheless, given that much greater Cu atoms were found per unit mass post-evaporation than post-filtration, this suggests an improvement in metal preservation and surface enrichment of CuOx species [6,8,21]. The wt% and at% Zn contents were significantly increased by the evaporation route, from 1.77 wt%/0.52 at% via the filtration method to 37.65 wt%/12.60 at% via the evaporation route. Correspondingly, Al decreased from 29.05 wt% to 4.71 wt%, while Si decreased from 14.73 wt% to 4.53 wt%. The large increase in Zn concentration as well as significant decrease in the support indicate that the evaporation preparation route effectively enhanced ZnO retention and surface availability compared to the filtration route. Similar improvements were seen for the Ni catalyst when it underwent evaporation-

assisted preparation. The wt% and at% Ni concentrations increased from 3.53 wt% and 1.07 at% via the filtration route to 21.44 wt% and 7.40 at% via the evaporation route. Additionally, the wt% of Al and Si decreased from 14.90 wt% to 2.85 wt%, and from 14.83 wt% to 2.84 wt%, respectively. Overall, these decreases suggest that NiO was preserved and dispersed better on the surface of the catalyst post-evaporation [6,8]. The presence of the metals (Mn, Cu, Zn and Ni) in the filtration-prepared composite catalyst were present at concentrations of 2.64 wt% (Mn), 3.97 wt% (Cu), 2.78 wt% (Zn), and 2.33 wt% (Ni). Evaporation treatment of the same samples altered these values slightly to 2.55 wt% (Mn), 2.18 wt% (Cu), and 3.38 wt% (Zn), and the Ni signal was below reliable quantitative detection under the selected analysis conditions. More importantly, the composition data show that the evaporation-treated composite catalyst had less contribution from the support phase, as evidenced by a decrease from 13.42 wt.% Al to 8.80 wt.%. Collectively, this indicates an enhanced level of integration and accessibility of the individual oxide phases present on the surface of the catalyst [33,34].

Collectively, the quantitative EDS data demonstrate that filtration resulted in some losses in either soluble metal precursors or very weakly absorbed metal precursors, while evaporation resulted in substantially higher retention rates and surface enrichments of the active metal-oxide phases. These results are consistent with all other analyses (FTIR, XRD, XPS, and adsorption performance), which indicate that the evaporation-prepared catalysts possess both enhanced structural properties and better sulfur-removal activities compared to those produced using filtration [6,32–34].

2.1.6. XPS Analysis of Catalysts Prepared by Filtration vs. Evaporation

XPS analysis was performed to evaluate the surface chemical states of the prepared catalysts and to investigate the influence of the solvent removal route on the surface composition of the deposited metal-oxide species, as shown in Figures 4 and 5. The presence or absence of significant halloysite-related peaks such as O 1s, Si 2p, and Al 2p are indicative of how much of the halloysite has been exposed. All these data collectively indicate that there is considerable variation in the distribution of active metals depending upon whether they have been removed by evaporation or filtration. Significant variations existed between the catalysts created using evaporation and filtration techniques. In general, the evaporation-prepared catalysts exhibited stronger and more distinguishable metal-oxide surface signals together with relatively reduced support-related contributions from Si 2p and Al 2p. Conversely, the filtration-prepared catalysts provided a significantly larger halloysite support signal compared to metal-oxide surface signals. This indicates that evaporation contributed to an increased surface exposure for the deposited metal-oxide phases as well as a more consistent distribution of these phases across the outer surface of the catalyst, while filtration resulted in a less representative surface presence of the active metal oxides.

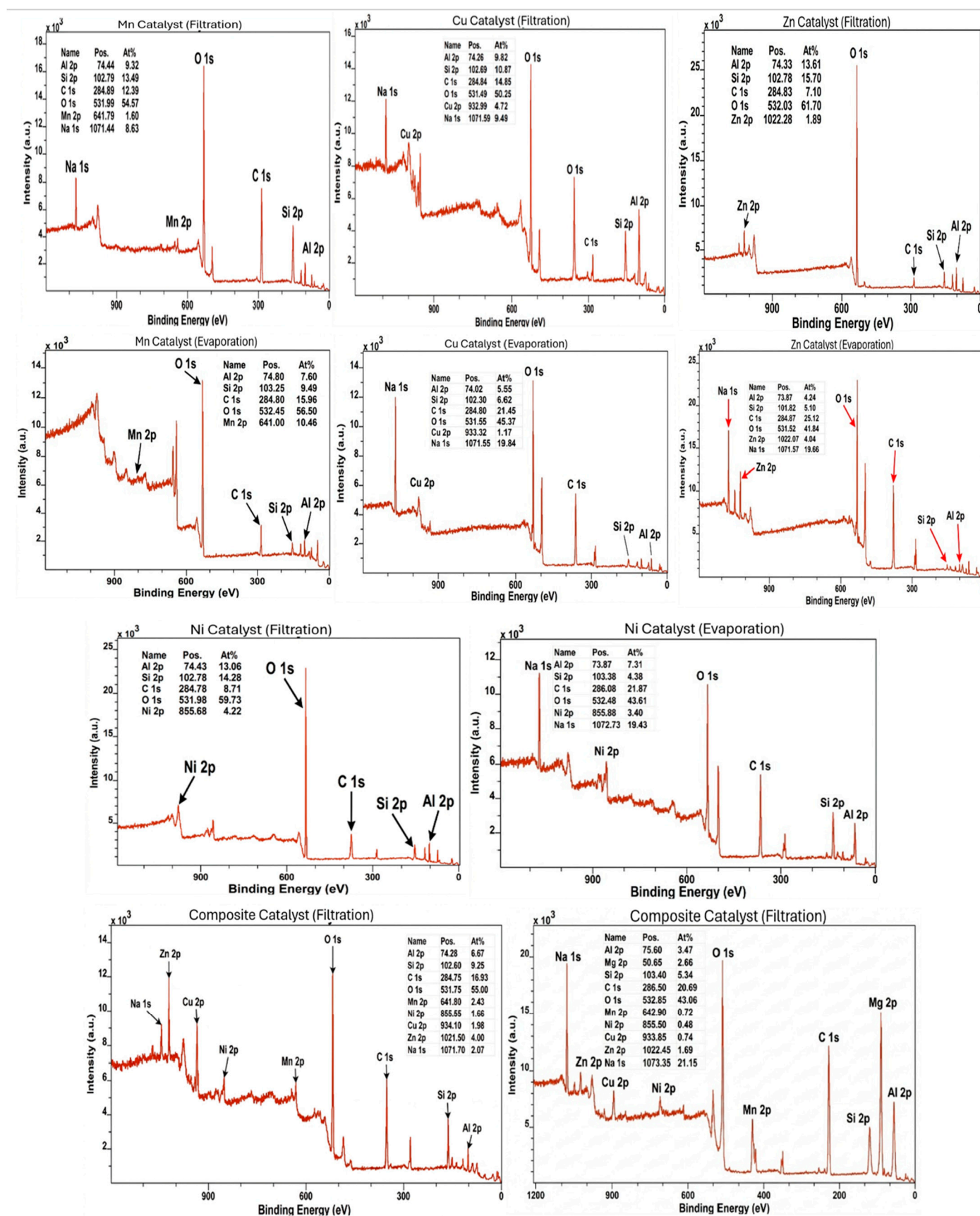


Figure 4. XPS spectra of catalysts prepared by filtration and evaporation methods.

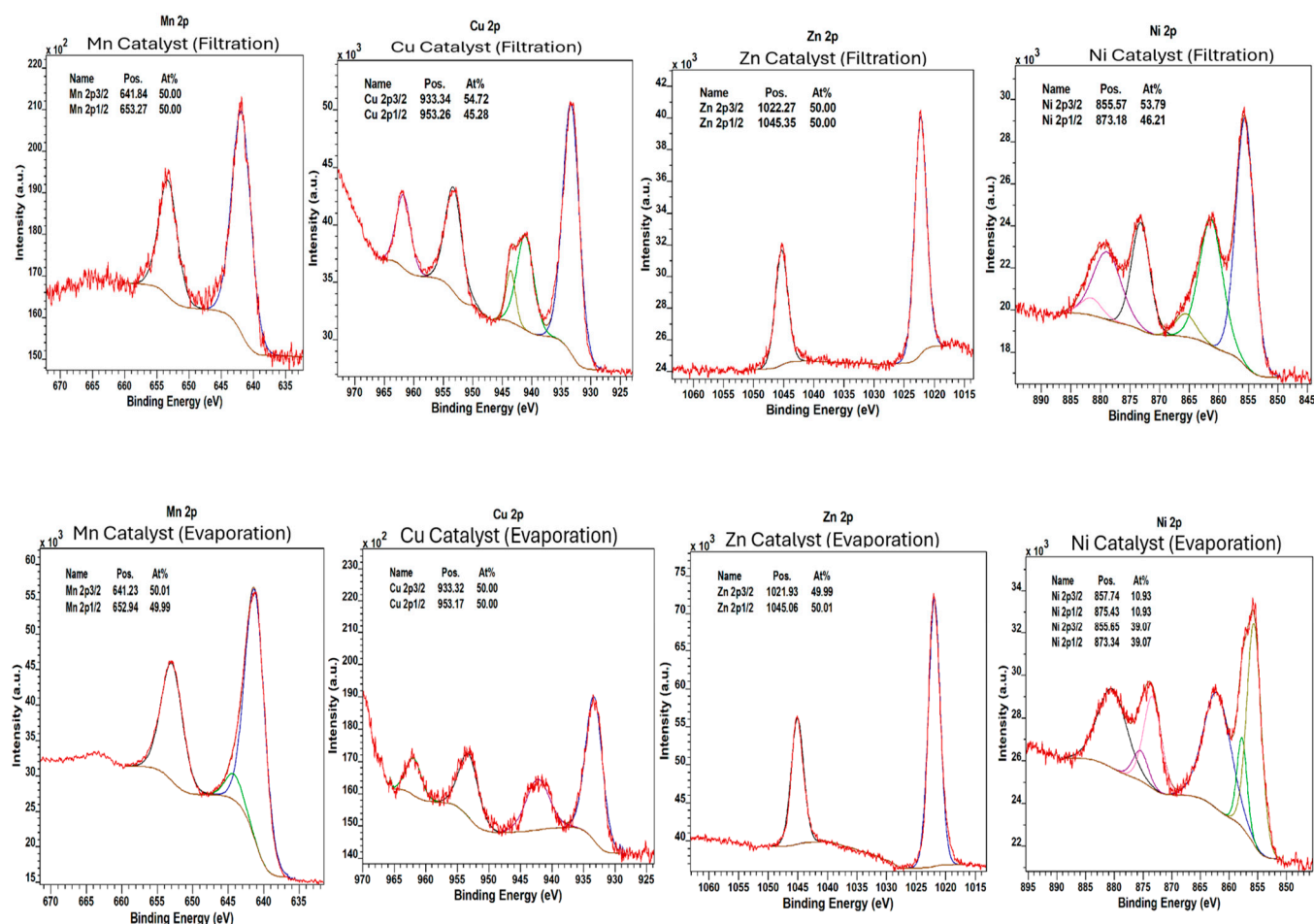


Figure 5. High-resolution XPS spectra (2p region) of single-metal catalysts.

For the Mn catalysts, the Mn 2p region showed peaks centered at approximately 641–643 eV for Mn 2p_{3/2} and 653–655 eV for Mn 2p_{1/2}. These binding energies are characteristic of manganese oxide species, primarily Mn²⁺/Mn³⁺ environments such as Mn₃O₄ and Mn₂O₃, rather than metallic Mn [37–39]. The O 1s peak observed near 531–533 eV further supports the presence of oxygen-containing manganese surface species. Although both preparation routes produced MnOx surface environments, the evaporation-prepared Mn catalyst exhibited a clearer and more intense Mn 2p signal relative to the support background than the filtration-prepared catalyst. In comparison, the filtration-prepared Mn catalyst displayed more prominent Si 2p and Al 2p signals, indicating greater exposure of the halloysite support surface. These observations suggest improved surface coverage and greater relative surface representation of MnOx species after evaporation-assisted preparation. For the Cu catalysts, the Cu 2p region showed the expected Cu 2p_{3/2} and Cu 2p_{1/2} near 933–935 eV and 953–955 eV, respectively. These binding energies are characteristic of oxidized copper species. However, because Cu⁺ and Cu⁰ possess similar Cu 2p_{3/2} binding energies, definitive distinction between these species requires Cu LMM Auger analysis and calculation of the Auger parameter. Therefore, the copper species were conservatively assigned as CuOx with possible Cu⁺/Cu²⁺ contributions, consistent with the CuO/Cu₂O phases observed by XRD [37,40,41]. The evaporation-prepared Cu catalyst exhibited stronger Cu-related surface features and comparatively lower support-related Si 2p and Al 2p contributions than the filtration-prepared Cu catalyst, indicating greater surface exposure of CuOx species after evaporation-assisted preparation. The Zn catalysts exhibited Zn 2p centered at approximately 1021–1023 eV for Zn 2p_{3/2} and 1044–1046 eV for Zn 2p_{1/2}. These values are characteristic of Zn²⁺ species associated with ZnO-type

environments [37,38]. No evidence of metallic Zn was observed, and the assignments were consistent with the ZnO reflections identified in the XRD patterns. Among all catalysts, the Zn system exhibited one of the most noticeable preparation-dependent differences. The evaporation-prepared Zn catalyst displayed a substantially stronger Zn 2p signal together with reduced Si 2p and Al 2p contributions relative to the filtration-prepared Zn catalyst, suggesting improved surface enrichment and accessibility of ZnO species after evaporation. For the Ni catalysts, the Ni 2p region displayed peaks near 855–856 eV for Ni 2p_{3/2} and 873–874 eV for Ni 2p_{1/2}, corresponding to Ni²⁺ species within NiO-like environments [37,42]. The broad Ni 2p envelope and associated satellite features are typical of nickel-oxide systems and support the formation of surface NiO species following calcination. These observations are also consistent with the NiO phases identified by XRD analysis. Like the other catalyst systems, the evaporation-prepared Ni catalyst exhibited a clearer Ni 2p signal relative to the halloysite background compared with the filtration-prepared Ni catalyst, indicating improved surface exposure of NiO species after evaporation-assisted preparation. The composite catalyst confirmed the simultaneous presence of Zn, Cu, Mn, Ni, O, Si, and Al on the catalyst surface. The metal core-level binding energies were consistent with oxide-type environments, including Zn²⁺, Ni²⁺, MnO_x, and CuO_x surface species. Although both preparation methods successfully produced mixed metal-oxide catalysts, the evaporation-prepared composite catalyst exhibited stronger and more balanced metal-oxide signals across the spectrum relative to the filtration-prepared catalyst. In contrast, the filtration-prepared composite catalyst showed comparatively stronger Si 2p and Al 2p contributions from the halloysite support. These observations suggest improved surface distribution and accessibility of the mixed oxide phases as a result of evaporation-assisted preparation.

Overall, the XPS results confirmed that the deposited active metals existed predominantly as surface oxide species after calcination rather than as metallic phases. More importantly, the analysis demonstrated that the solvent removal method significantly influenced the surface chemical environment of the catalysts. Evaporation-prepared catalysts consistently produced stronger and more distinguishable surface oxide signals compared with filtration-prepared catalysts, indicating improved surface exposure and distribution of the active oxide phases. These findings are fully consistent with the EDS, FTIR, XRD, and adsorption performance results, which collectively demonstrate superior structural properties and sulfur-removal performance of the evaporation-prepared catalysts.

2.2. Analysis of Catalyst Adsorption Performance

The adsorption of sulfur by catalysts made through both filtration and evaporation was studied using breakthrough tests at a 10 ppm sulfur content (the breakpoint), as shown in Figure 6. The breakthrough curve indicated that the preparation process greatly affected the performance of the catalysts, regardless of the catalyst's composition. All catalysts (evaporation method) exhibited a greater delay in sulfur breakpoint than those prepared via filtration. Therefore, it can be concluded that the route used to remove the solvent from the catalyst strongly influences the final effectiveness and accessibility of the active surface of the catalyst. The observed trend is consistent with theories for preparing supported catalysts, which indicate that the methods employed for drying and removing solvents can influence the redistribution of precursors during calcination, oxide formation, and metal retention, as well as the ultimate surface accessibility [7–9,21]. The improvement in adsorption behavior of the catalysts produced through evaporation is potentially due to the synergistic effects from various parameters, as shown from characterization studies. EDS analysis indicated greater surface-associated concentrations of the active metal-oxide species for the evaporation-prepared catalysts relative to the filtration-prepared systems. It is believed that evaporation resulted in lower or no loss of dissolved

precursors during removal of the solvent (evaporated) relative to physical separation (filtration) of the solvent. XPS analysis showed more distinguishable surface oxide features for the evaporation-prepared catalysts relative to the filtration-prepared systems, indicating greater surface exposure of the active oxide environments. The XRD results support similar conclusions about the development of oxide phases and dispersion of these phases within evaporation-produced materials. Additionally, SEM showed more fracturing, porosity, and surface roughness in the morphology of particles of the evaporation-prepared catalysts, whereas filtration-prepared catalysts had smoother and more compact particle morphology. Similarly, BET surface areas of both types of catalysts exhibited different levels of porosity. However, the results of this study suggest that adsorption performance was not governed solely by total surface area or pore structure. Instead, the combined effects of accessible pore architecture, surface exposure of MnOx, CuOx, ZnO, and NiO species, and the availability of chemically active surface oxide environments appeared to play more significant roles in sulfur adsorption performance.

The Mn catalyst made using evaporation outperformed the other single-metal systems tested by demonstrating over four times greater overall sulfur adsorption, with a breakthrough occurring at 1410 min versus a mere 240 min for Mn catalysts made via filtration, as shown in Figure 6. The Mn catalyst produced by evaporation had nearly five times the surface area of the filtration sample (43.308 m²/g vs. 10.833 m²/g) along with roughly 2.5 times the total pore volume (0.223 cm³/g vs. 0.091 cm³/g). Therefore, it is logical to conclude that there were significantly more active adsorption sites available on the evaporation-produced Mn catalyst. Furthermore, SEM imaging demonstrated a more open and fractured morphology for the evaporation-produced Mn catalyst, while XPS analysis indicated a stronger Mn surface signal due to manganese being primarily present as Mn²⁺/Mn³⁺/Mn⁴⁺oxide. Also, the XRD data indicate that the MnOx formed during evaporation was dispersed across the surface more evenly, and did not have large crystallites such as those seen in the filtration-produced Mn catalyst. Thus, taken together, the characterization data demonstrate that the increased Mn breakthrough rate observed in this study was a direct result of a combination of factors, including increased Mn retention, increased oxide availability for adsorption, and an optimal surface structure for MnOx adsorption sites. These are consistent with what is known about manganese oxide's ability to bind sulfur-containing molecules and their redox properties that allow them to use surface-bound oxygen atoms to facilitate additional sulfur binding through adsorption mechanisms [43,44].

The Cu catalyst demonstrated an equally impressive increase in breakthrough time when comparing the evaporation-prepared samples to those prepared using filtration. Specifically, as seen in Figure 6, the evaporation-prepared Cu catalyst achieved breakthrough at about 1350 min, whereas the Cu catalysts prepared through filtration were able to achieve breakthrough at only 215 min. Therefore, the significant increase in the time to reach breakthrough indicates that there was a substantially more effective sulfur adsorbent on the surface of the Cu evaporation catalyst. The data from structural and chemical characterization techniques support these findings. Specifically, BET analysis showed that evaporation enhanced both the surface area (18.292 m²/g vs. 9.651 m²/g) and pore volume (0.125 cm³/g vs. 0.076 cm³/g) of the Cu catalyst. Additionally, SEM images demonstrate a more accessible, roughened morphology of the evaporation-prepared sample. Furthermore, XRD showed evidence of more developed CuO-related features in the evaporation-prepared sample and XPS demonstrated a significantly increased Cu surface signal indicative of oxidized Cu⁺/Cu²⁺ species. Finally, EDS demonstrated that a larger amount of Cu was present in the evaporation-prepared catalyst compared to its corresponding filtration-prepared counterpart, thereby demonstrating that losses of precursors during filtration decreased the quantity of Cu-based active sites available for reaction. Consistent with

the previous observations, the FTIR results also demonstrate stronger interactions between Cu and O/surface oxygen within the pores of the evaporation-prepared catalyst. Overall, it can be concluded that the increased Cu breakthrough performance of the evaporation-prepared catalyst relative to that prepared via filtration can be attributed to increased retention of Cu, more developed Cu oxides, and increased accessibility of the pore structure.

The evaporation process helped the Zn catalyst as well, although the advantage from evaporation was less in comparison to Mn and Cu; the evaporation-produced Zn catalyst achieved breakthrough at 480 min versus 205 min for the filtration-produced Zn catalyst. The importance of this increase is furthered due to the fact that the Zn system illustrates that sulfur adsorption does not solely rely on BET surface area. It is true that the evaporation-produced Zn catalyst had a lower BET surface area ($14.034 \text{ m}^2/\text{g}$) and pore volume ($0.096 \text{ cm}^3/\text{g}$), whereas the filtration-produced Zn catalyst had a higher BET surface area ($38.769 \text{ m}^2/\text{g}$) and pore volume ($0.213 \text{ cm}^3/\text{g}$). However, when comparing their respective performances, there was a substantial improvement in performance for the evaporation-produced Zn catalyst. The evidence indicates that the primary difference between the two Zn samples is that evaporation created a significantly larger mean pore diameter ($274.758 \text{ \AA}$) for the evaporation-produced Zn catalyst in addition to retaining a stronger Zn surface presence. Additionally, XPS indicated a stronger Zn 2p signal for the evaporation-produced Zn catalyst, suggesting greater Zn^{2+} surface retention of Zn species. Furthermore, XRD demonstrated more clearly defined ZnO-related peaks for the evaporation-produced Zn catalyst. Lastly, SEM demonstrated an open and brittle structure for the evaporation-produced Zn catalyst. Overall, these findings demonstrate that the increased performance of the Zn evaporated catalyst was not due to having a larger total BET surface area, but rather due to better pore accessibility and a more effective ZnO-rich active surface.

Ni was the least effective of all single-metal systems tested; however, the differences among the routes were significant. The evaporation-prepared Ni catalyst required 60 min to reach a breakthrough point compared to 30 min for the filtration route. While the overall effectiveness of Ni was significantly less than that of Mn, Cu, and Zn, the evaporation route provided approximately a two times longer useful life of the catalyst. Again, this demonstrates a superior preservation of the active phase. A higher level of Ni was observed on the surface of the evaporated sample using XPS, as evidenced by a slightly greater Ni surface signal. XPS also found most of the Ni in the form of Ni^{2+} oxides. XRD found similar levels of NiO-related peaks in both samples, with some indication of finer oxide particles formed from the evaporation process. A comparison of SEM images revealed a rougher and more structurally heterogeneous surface morphology for the evaporation-prepared sample. In addition, BET measurements showed a larger average pore diameter (222.430 vs. $165.525 \text{ \AA}$) in the evaporated sample, although it also showed lower values for total surface area and pore volume. Therefore, these results demonstrate that while accessibility of the active sites and the chemical quality of those sites are more important than BET surface area alone, there appears to be some intrinsic limitations based upon the properties of the Ni-based oxide surface with respect to sulfur adsorption chemistries under current test conditions.

The evaporation method was beneficial to the composite catalyst. In comparison to the composite made using the filtration process which achieved breakthrough at approximately 300 min, the composite made by evaporation took approximately 480 min to achieve breakthrough. Overall better metal retention was evidenced by EDS for the composite made via evaporation. Further, it was shown by XPS that there were enhanced surface signatures from Zn^{2+} , $\text{Cu}^+/\text{Cu}^{2+}$, Ni^{2+} , and $\text{Mn}^{2+}/\text{Mn}^{3+}$ species for the composite prepared via evaporation relative to that of the composite prepared using filtration. Similar overlapping mixed oxide diffraction lines are seen in the two samples; however, there

were more defined and dispersed oxide phases present in the evaporation-prepared sample. A higher degree of porosity and fracturing was noted for the composite prepared via evaporation. BET analysis provided evidence of higher pore volumes (0.133 vs. 0.096 cm³/g) and larger average pore sizes (241.840 vs. 172.030 Å), despite a smaller surface area.

The key findings of this study, taken as a whole, have led to an overall mechanistic understanding of the process. The evaporation method produced better-performing catalysts because it maintained a greater percentage of active metal precursors attached to the support throughout the synthesis process and permitted them to remain in contact with the support after the solvents had been removed, thus providing conditions favorable to the complete oxidation of the precursor material and its even distribution over the accessible surface areas of the support. In comparison, filtration caused a physical separation of the liquid from the solid prior to complete retention and conversion of the dissolved metal precursors into reactive metal-oxide surface species. Thus, less metal was available at the surface for sulfur adsorption, and there existed shorter adsorption lifetimes. These interpretations are heavily reinforced by collective data obtained with EDS, XPS, XRD, SEM, BET, and FTIR. One of the major conclusions drawn from this research is that the catalysts exhibiting the greatest sulfur-removal efficiencies did not necessarily possess the largest BET surface areas; instead, they were characterized by their more extensive and chemically active metal-oxide surfaces. For example, when comparing the Zn, Ni, and composite systems prepared using either evaporation or filtration techniques, it was found that those prepared via evaporation exhibited greater removal efficiencies than those prepared using filtration techniques regardless of whether they possessed higher or lower BET surface areas. Consequently, while geometric areas (i.e., total areas) played a role in determining how much sulfur could be adsorbed onto these materials, it was not the primary determinant. Rather, the effectiveness of each preparation technique in preserving and exposing surface MnOx, CuOx, ZnO, and NiO active oxide environments, which are responsible for sulfur adsorption through metal–sulfur interactions and surface redox processes, appeared to determine the overall sulfur-removal efficiency.

Ethyl mercaptan removal over the prepared metal-oxide materials is proposed to occur through a combination of adsorption and surface redox-assisted interactions. The sulfur atom in CH₃CH₂SH adsorbed onto exposed MnOx, CuOx, ZnO, and NiO surface sites through metal–sulfur affinity, while surface oxygen species associated with these oxides facilitate sulfur capture. In particular, the redox-active MnOx and CuOx phases may promote partial oxidation of adsorbed mercaptan intermediates into more strongly bound surface sulfur species, thereby enhancing sulfur removal. Consequently, the effectiveness of the process depends not only on the total BET surface area but also on the availability and accessibility of surface metal-oxide sites, pore accessibility, and the chemical nature of the oxide surface. The superior breakthrough performance observed for the evaporation catalysts is therefore attributed to their more favorable surface oxide environments, as supported collectively by the BET, FTIR, XRD, EDS, and XPS characterization results. Similar adsorption and redox-assisted sulfur removal mechanisms have been reported previously for transition metal-oxide desulfurization systems [4,35,36,43,44].

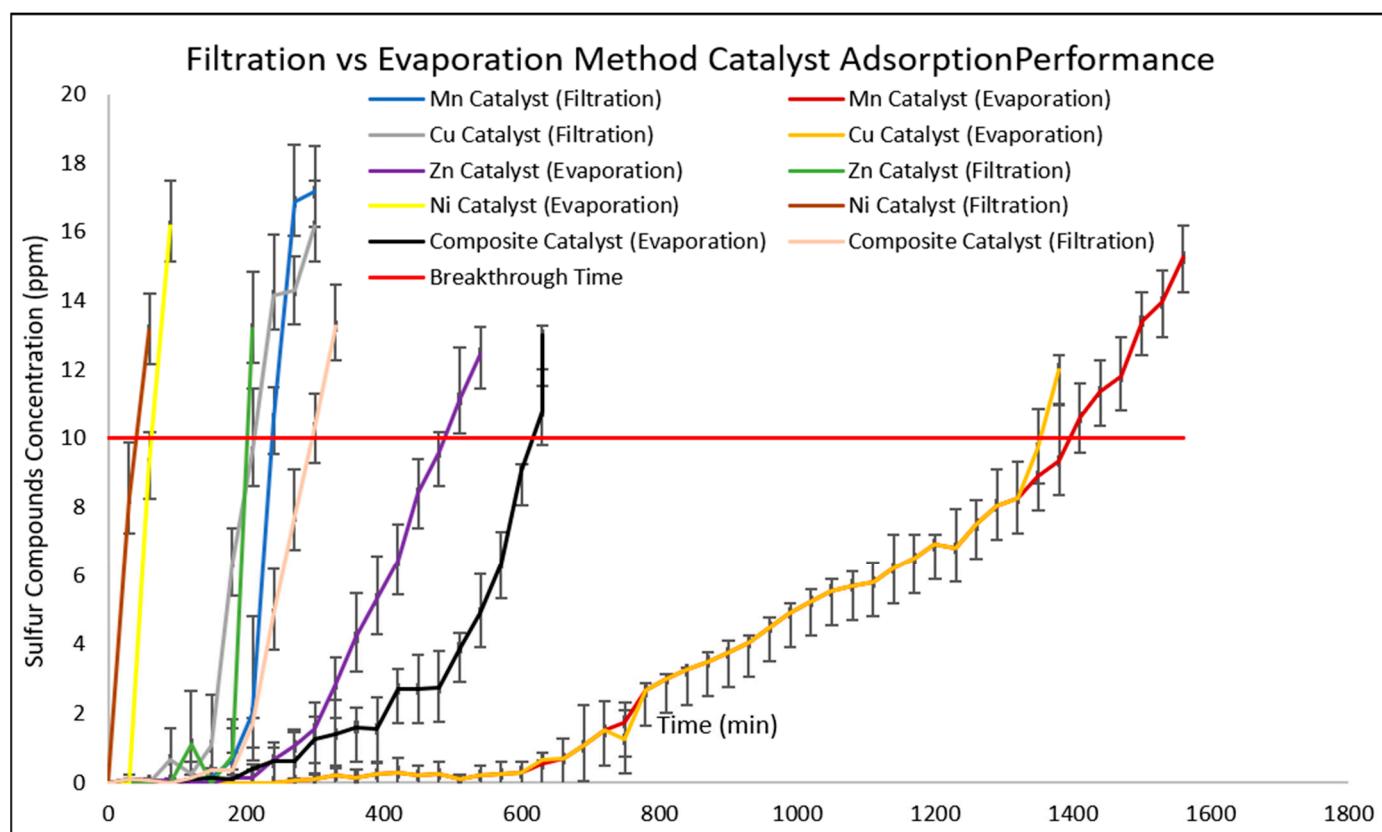


Figure 6. Catalyst adsorption performance.

Evaporation-derived Mn and Cu catalysts outperformed the commercial benchmark catalyst. Under equivalent experimental conditions, Mn and Cu catalysts were able to achieve longer breakthrough times than the commercial benchmark catalyst, as shown in Figure 7 and Table 3. Mn and Cu catalysts achieved longer breakthrough times of 1410 min and 1350 min, respectively, in comparison to a commercial benchmark catalyst breakthrough time of 1200 min. In terms of percentage increase over the commercial benchmark catalyst, the breakthrough time of Mn catalysts increased by 17.5%, while Cu catalysts had an increase of 12.5%. The commercial benchmark catalyst also showed less ability to adsorb sulfur than Mn and Cu evaporation catalysts. The amount of adsorbed sulfur on a mass basis for the commercial benchmark catalyst was 43.8 mg S/g. Mn and Cu catalysts demonstrated the ability to adsorb more sulfur prior to becoming exhausted at amounts of 51.5 mg S/g and 49.3 mg S/g, respectively.

Table 3. Performance summary of the best catalysts and the commercial benchmark catalyst.

Catalyst	Breakthrough Time (Minutes)	% Change	Sulfur Capacity, q mg S/g
Commercial	1200	0%	43.8
Mn	1410	17.5%	51.5
Cu	1350	12.5%	49.3

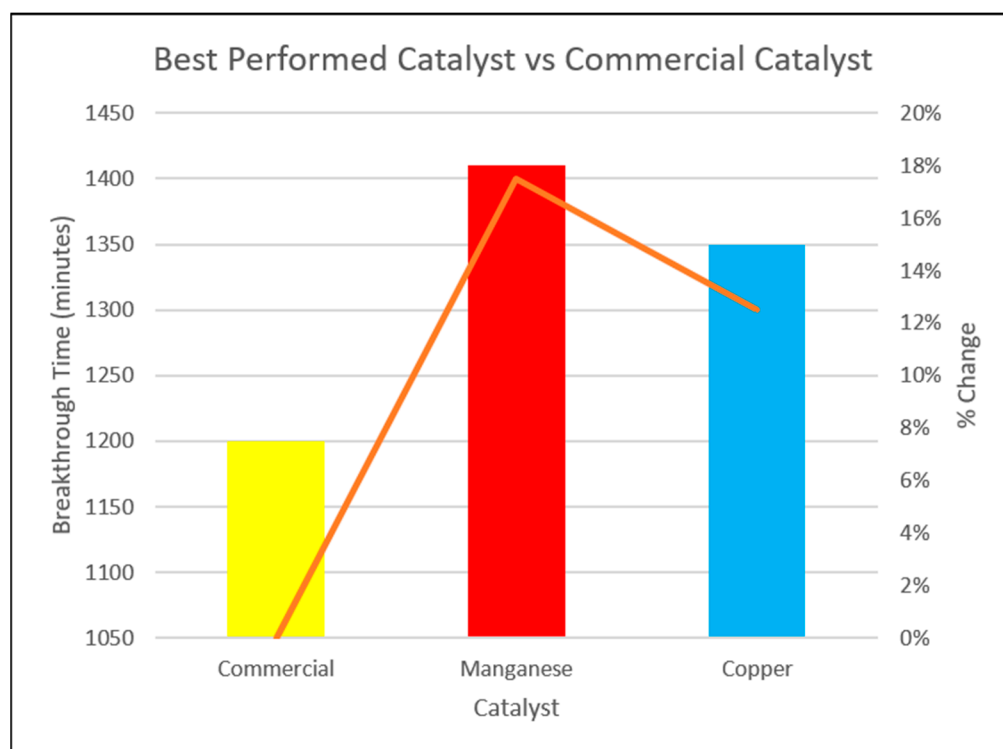


Figure 7. Performance comparison of the prepared catalysts (evaporation method) versus the commercial catalyst.

The findings represent a significant development in terms of practical application since the enhanced performance resulted from an easy to implement and cost-effective synthesis process based on solvent evaporation prior to calcination. The use of solvent evaporation prior to calcination represents a significantly simpler and less expensive approach to manufacturing catalysts compared to many current commercial methods used in the manufacture of catalysts for industrial applications. Therefore, the Mn and Cu catalysts made with the evaporation method exhibit great promise as economical and scalable substitutes for the commercial benchmark catalyst for trace sulfur removal from natural gas streams. Additionally, longer breakthrough times and greater sulfur capacity in industrial fixed-bed desulfurization processes are beneficial since longer catalyst service lives can result in less frequent replacement, increased reliability in fixed-bed operations, and better protection for downstream sulfur-sensitive equipment.

Table 4 compares the performance of the evaporation-prepared halloysite-supported metal-oxide catalysts developed in this work with representative sulfur-removal materials reported in the literature. Although direct comparison is limited by differences in sulfur compounds, operating conditions, and removal mechanisms (adsorption versus oxidative desulfurization), the results demonstrate that the evaporation-prepared Mn and Cu catalysts exhibit competitive performance under high-pressure natural gas conditions. Notably, the Mn catalyst achieved a sulfur adsorption capacity of 51.5 mg S/g with a breakthrough time of 1410 min, exceeding both the commercial benchmark catalyst (43.8 mg S/g; 1200 min) and the reported Ni-Ti-LDH adsorbent for ethyl mercaptan removal. These comparisons demonstrate that optimizing the solvent-removal step during catalyst preparation provides a simple and effective strategy for improving the sulfur-removal performance of halloysite-supported metal-oxide materials.

Table 4. Comparison of the sulfur-removal performance of the catalysts developed in this work with representative materials reported in the literature.

Material/System	Target Sulfur Compound	Removal Method	Operating Conditions	Performance Metric	Reference
Commercial benchmark catalyst	Ethyl mercaptan	Fixed-bed adsorption/re-dox-assisted sulfur removal	25 °C, 200 psi, 36 mL/min, 200 ppm ethyl mercaptan/CH ₄	1200 min breakthrough; 43.8 mg S/g catalyst	This work
Mn/halloysite prepared by evaporation	Ethyl mercaptan	Fixed-bed adsorption/re-dox-assisted sulfur removal	25 °C, 200 psi, 36 mL/min, 200 ppm ethyl mercaptan/CH ₄	1410 min breakthrough; 51.5 mg S/g catalyst	This work
Cu/halloysite prepared by evaporation	Ethyl mercaptan	Fixed-bed adsorption/re-dox-assisted sulfur removal	25 °C, 200 psi, 36 mL/min, 200 ppm ethyl mercaptan/CH ₄	1350 min breakthrough; 49.3 mg S/g catalyst	This work
NH ₄ F-HKUST-1	BT/DBT/4,6-DMDBT	Adsorption desulfurization	25 °C, 1000 ppm sulfur in model oil, 1 h	23.8 mg S/g (BT), 46.8 mg S/g (DBT), 36.8 mg S/g (4,6-DMDBT)	[45]
UiO-66(Zr/Sn ²⁺)	Dibenzothiophene (DBT)	Oxidative desulfurization	60 °C, H ₂ O ₂ oxidant	100% DBT removal within 20 min	[46]
Ni-Ti-LDH nanosheets	Ethyl mercaptan	Adsorption/separation from methane	298 K, GHSV = 12,000 h ⁻¹	49.41 mg ethyl mercaptan/g adsorbent	[2]

3. Materials and Methods

3.1. Materials

The chemicals used in the experiments include zinc acetate dihydrate (97%), nickel (II) acetate tetrahydrate (99%), copper (II) nitrate trihydrate (99%), and manganese acetate tetrahydrate (98%). Additional reagents include sodium hydroxide and 200-proof ethanol. All chemicals were purchased from Fisher Scientific (Fisher Scientific, Waltham, MA, USA) except the halloysite support, which was purchased from Coastal Chemicals in Louisiana, USA. The use of halloysite as a catalyst support is based on its unique naturally occurring aluminosilicate nanotubular structure that provides both an external siloxane surface (Si-O-Si) and an internal aluminol lumen (Al-OH). The unique combination of physical and chemical properties exhibited by halloysite make it a logical choice for the design of highly efficient metal-oxide catalysts for the removal of sulfur-containing compounds from natural gas [10].

3.2. Catalyst Preparation

All chemicals were of reagent-grade quality and used without further purification. The catalysts prepared in this study as shown in Figure 8 were made through via the wet impregnation–reflux technique. This process is intended to provide an even distribution of metal oxides over the halloysite surface and at the same time retain the physical properties of the halloysite. Raw halloysite was first crushed and sifted with a 40-mesh sieve to create particles that averaged about 0.4 mm in diameter. Halloysite weighing a total of 3 g was then mixed in 120 mL of 99.5% ethanol to make a homogeneous solution (solution 2) for sonication. Sonication is widely reported to improve the dispersion of metal precursors on porous supports by reducing particle agglomeration, enhancing interfacial contact, and promoting more uniform deposition of active species [11,12].

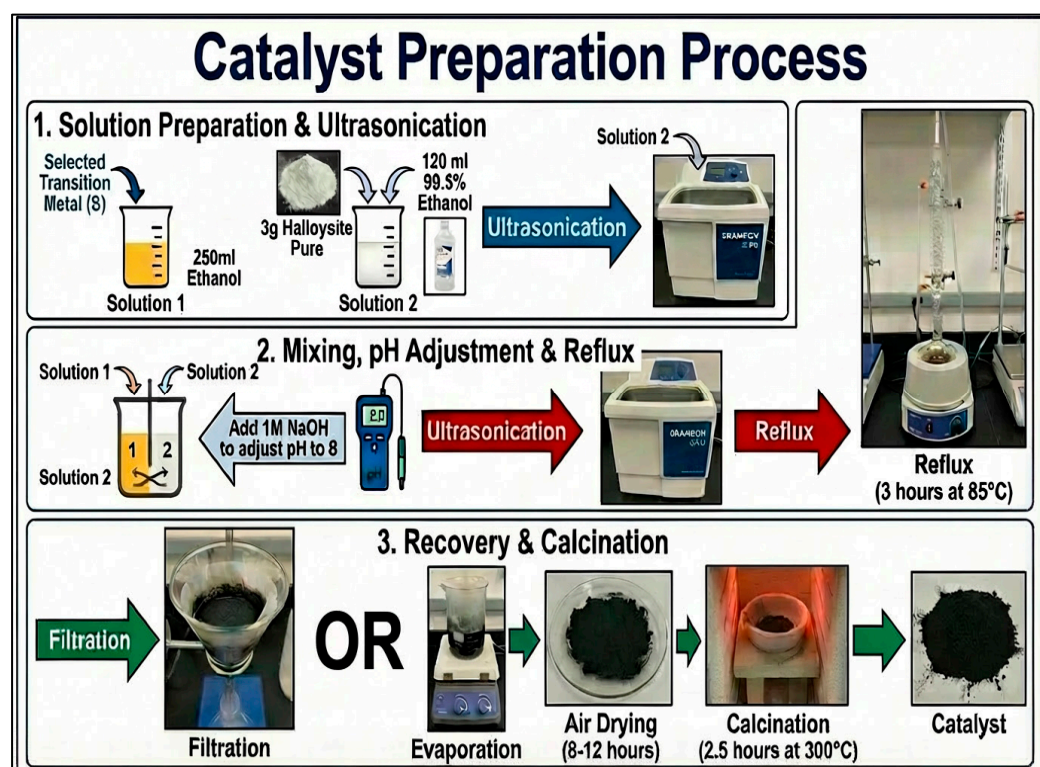


Figure 8. Catalyst preparation methods.

A separate precursor solution for transition metals was prepared by dissolving 1.5 g of the selected metal(s) in 240 mL of 99.5% ethanol. To create Solution 1, the appropriate individual metal salt(s) (Zn, Cu, Mn, Ni) for the particular catalyst formulation were added. The amount of metal salt(s) added to Solution 1 as shown in Figure 8 was determined from the desired metal loading and weight percent of the metal content. Since ethanol can effectively dissolve metal precursors without excessive pre-hydrolysis and allows for control over the rate of metal deposition onto the alumina support, ethanol was chosen as the solvent [13]. Once Solution 1 had been formed, it was slowly added to Solution 2. The pH of the mixed solution was gradually adjusted to approximately 8 by drop-wise addition of 1 M NaOH under continuous magnetic stirring and monitored using a calibrated digital pH meter. Ultrasonication was carried out for 30 min at 200 W to ensure homogeneous dispersion of the halloysite support and metal precursor solution. By maintaining an alkaline environment, conditions were created that allowed for the precipitation of intermediate metal-hydroxide compounds. These metal-hydroxide intermediate compounds were transformed into metal-oxide materials upon reflux and calcination. The addition of NaOH as a precipitation agent has long been recognized as effective in promoting the immobilization of metal species onto aluminosilicate support via electrostatic forces and by providing sites for the nucleation of metal species on surface hydroxyl groups [13]. Following the mixing of the two solutions, it was ultrasonically dispersed to facilitate uniform distribution of metal species throughout the internal pore volume of the halloysite mineral. The suspension was then refluxed at 85 °C for 3 h to enable deposition and reaction of the metal species with the support. Refluxing facilitates the diffusion of metal ions into the halloysite lumen and aids in creating strong metal–support bonds; these bonds are essential to the stability of the catalyst [14]. After reflux, the resulting solids were removed from the liquid phase via filtration or evaporation methods. For the evaporation method, solvent removal was carried out at approximately 85 °C under continuous stirring until complete ethanol evaporation was achieved. For the filtration method, vacuum filtration was performed using Whatman filter paper (from Fisher

Scientific, Waltham, MA, USA). The solids were dried under air for 8–12 h and then calcined at 300 °C for 2.5 h. The calcination process converts the metal-hydroxide species that have been deposited on the support into their respective metal oxides. Additionally, the calcination process stabilizes the structural framework of the catalyst. The calcination process is conducted at a relatively low temperature as it enables the production of the necessary metal oxides and minimizes the sintering of the metal particles, thereby maintaining the surface area of the support [15]. BET, FTIR, XRD, SEM-EDS, and XPS characterization analyses were performed at the University of Louisiana at Lafayette and at the Louisiana State University at Baton Rouge research characterization facilities using standard operating procedures associated with each instrument system.

3.3. Characterization Methods

The physicochemical properties of the prepared catalysts were characterized using multiple analytical techniques to evaluate their textural properties, structural characteristics, surface morphology, elemental composition, crystalline phases, and surface chemical states.

The specific surface area, pore volume, and average pore-size distribution of the prepared catalysts were determined by nitrogen adsorption–desorption analysis using a Micromeritics ASAP 2020 surface area and porosity analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA). Prior to analysis, approximately 0.2–0.3 g of each sample was degassed under vacuum at 120 °C for 12 h to remove physically adsorbed moisture and impurities. Surface area was calculated using the Brunauer–Emmett–Teller (BET) method, while pore-size distribution was determined using the Barrett–Joyner–Halenda (BJH) method.

Surface functional groups and chemical bonding environments were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) on a Thermo Scientific Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Spectra were recorded over the wavenumber range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1} , using 32 scans per sample under ambient conditions.

The crystalline phases of the prepared catalysts were analyzed using X-ray Diffraction (XRD) on a Bruker D8 Advance diffractometer (Bruker Corporation, Billerica, MA, USA) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 40 mA. Diffraction patterns were collected over a 2θ range of 10–80° with a step size of 0.02° and scanning rate of 2°/min. Surface morphology was examined using Scanning Electron Microscopy (SEM) on a JEOL JSM-6610LV scanning electron microscope (JEOL Ltd., Tokyo, Japan). Imaging was performed under an accelerating voltage of 10–20 kV depending on sample conductivity and image resolution requirements. Elemental composition analysis was performed using an Oxford Energy Dispersive X-ray Spectroscopy (EDS) detector attached to the SEM system, and both weight percentage (wt%) and atomic percentage (at%) of detected elements were recorded.

Surface elemental composition and oxidation states of the prepared catalysts were analyzed using X-ray Photoelectron Spectroscopy (XPS) on a Kratos AXIS Ultra DLD spectrometer (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromatic Al K α X-ray source (1486.6 eV) operating under ultra-high vacuum conditions. Spectra were collected over a binding energy range of 0–1200 eV, and charge correction was referenced using the adventitious carbon C 1s peak at 284.8 eV.

All characterization analyses were conducted at the research characterization facilities of the University of Louisiana at Lafayette, LA, and Louisiana State University, Baton Rouge, LA, USA, using calibrated instruments and standard operating procedures associated with each respective analytical technique.

3.4. Catalyst Testing Process

The sulfur-removal performance test, as shown in Figure 9, was carried out in a stainless-steel tube packed-bed reactor with dimensions of 310 mm (length) and an inner diameter of 6.35 mm. In each experimental run, 0.5 g of catalyst was loaded into the central section of the reactor and held in place using glass wool within the reactor. Therefore, the full reactor length does not represent the effective packed catalyst bed length. Before testing, the reactor was pressurized with nitrogen at 60 psi at 36 mL/min and leak-tested using Snoop™ leak detector solution (Swagelok Company, Solon, OH, USA), followed by a 30 min pressure-hold test to confirm system integrity. A negligible pressure drop was observed before switching to the sulfur-containing feed gas. This enabled leak testing of all connections, from the gas tank to the downstream mass flow controller. Once the system was found to be leak-free, to start the sulfur compound removal process, the feed was changed from N₂ (99.99%) to a gas mixture with 200 ppm ethyl mercaptan in methane. The feed gas consisted of 200 ppm ethyl mercaptan balanced in high-purity methane (≥99.98%). The gas combination was introduced axially into the packed-bed reactor at 25 °C, 200 psi, and 36 mL/min. The operating conditions (200 psi and 36 mL/min) were selected based on previous studies, where these parameters provided stable flow conditions and optimal adsorption performance for similar catalyst systems. The use of near-ambient temperature (25 °C) was chosen to reflect energy-efficient and economically favorable operating conditions for practical applications. Temperature during adsorption testing was continuously monitored and controlled using a K-type thermocouple connected to a digital temperature controller to ensure stable operating conditions throughout the experiments. The nominal gas hourly space velocity (GHSV) was approximately 220 h⁻¹, calculated based on the total reactor internal volume and the inlet volumetric flow rate. Once the flow was stabilized at the set pressure, the GC-MS (GC (model:6890N)-MS (model:2614A), Agilent Technologies, Santa Clara, CA, USA) procedure began immediately. Breakthrough data were collected once a breakthrough (10 ppm) was attained. Breakthrough was defined at an outlet concentration of 10 ppm total sulfur, expressed on a sulfur-equivalent basis from ethyl mercaptan. This threshold corresponds to approximately 5% of the inlet concentration (200 ppm), and was selected as a conservative limit relative to typical natural gas pipeline specifications (16–20 ppm total sulfur), while remaining within the reliable detection range of the GC-MS and consistent with values reported in desulfurization studies. This definition ensures that the reported breakthrough times are directly relevant to industrial sulfur limits [16,17]. The sulfur adsorption capacity (q) at breakthrough was calculated using Equation (1):

$$q = \frac{Q}{M} \int_0^t (C_i - C_f) dt, \quad (1)$$

where Q is the volumetric flow rate (m³/min), M is the mass of the catalyst (g), C_i and C_f are the inlet and outlet sulfur concentrations (mg/m³), and t is the breakthrough time (minutes).

The volumetric flow rate was converted from mL/min to m³/min, and the inlet concentration of CH₃CH₂SH (ppm) was converted to mass concentration (mg/m³) using the ideal gas relationship. This approach ensures consistent units and allows for the accurate calculation of sulfur capacity in mg S/g catalyst.

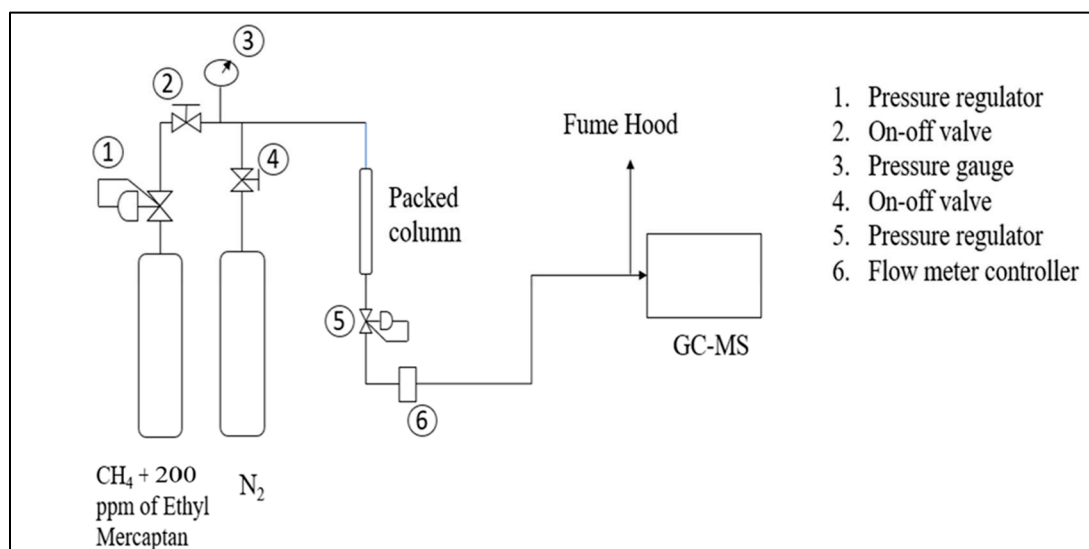


Figure 9. Catalyst adsorption performance experimental setup.

4. Conclusions

The present study demonstrated that the catalyst preparation route significantly influenced the structural properties, surface chemistry, and sulfur-removal performance of halloysite-supported metal-oxide catalysts. Compared with filtration, the evaporation-assisted preparation method consistently produced catalysts with greater surface exposure of MnO_x, CuO_x, ZnO, and NiO species, improved structural heterogeneity, and enhanced accessibility of the active oxide environments. The combined BET, SEM, EDS, XRD, FTIR, and XPS results show that evaporation minimized precursor loss during synthesis and promoted better preservation and distribution of the active surface oxide phases on the halloysite support. In contrast, filtration resulted in comparatively lower surface oxide representation due to partial removal of soluble or weakly attached precursor species during processing.

Among the prepared catalysts, the evaporation-prepared Mn and Cu catalysts exhibited the best sulfur-removal performance, achieving breakthrough times of approximately 1410 min and 1350 min, respectively, compared with 1200 min for the commercial benchmark catalyst under identical testing conditions. The improved performance of the Mn and Cu systems was attributed to the greater surface accessibility of MnO_x and CuO_x active oxide environments, together with improved interaction between the metal-oxide phases and the halloysite support after evaporation-assisted preparation. These surface oxide environments likely enhanced sulfur adsorption through stronger metal–sulfur interactions and redox-assisted adsorption processes. Overall, the results demonstrate that evaporation provides a simple, scalable, and effective preparation strategy for producing high-performance halloysite-supported metal-oxide sulfur-removal catalysts. These materials show strong potential for industrial natural gas desulfurization involving trace sulfur compounds such as ethyl mercaptan. Although catalyst regeneration and recyclability were not investigated within the scope of the present study, Future work will specifically investigate catalyst regeneration efficiency, cyclic stability, and long-term industrial applicability under repeated adsorption–desorption cycles.

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