Influence of chalcopyrite removal and mechanical exfoliation on the performance of molybdenite catalysts supported on activated bauxite for alcohol synthesis by Fischer-Tropsch process

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Abstract

The top-down approach was used to develop catalysts for higher alcohol synthesis by starting with low-grade molybdenite concentrate and mesoporous activated bauxite as the active metal and support, respectively. The results of the study showed that the process of chemical leaching significantly reduced copper in the form of chalcopyrite in the concentrate by over 95%. This reduction in copper content of purified catalysts led to an increase in the selectivity for C3+ alcohols compared to catalysts based on impure molybdenite. Additionally, the process of exfoliation not only reduced the particle size of the active component but also increased the selectivity for C3+ alcohols and the conversion of CO. The chemical-mechanical activation process developed in this study resulted in an improvement in catalyst activity of more than 50%.

A R T I C L E   I N F O

A B S T R A C T

Keywords:
- Molybdenite-based catalyst
- Activated bauxite
- Alcohol synthesis
- Chemical activation
- Mechanical exfoliation

1. Introduction

As a consequence of population growth, the world’s demand for energy has increased drastically [1]. This surge in demand necessitates the development of cost-effective and environmentally benign ways to conserve the planet’s limited natural resources and protect the environment. The Fischer-Tropsch (FT) process can be considered a useful method for the synthesis of liquid fuels (without aromatics and sulfur) from syngas as an eco-friendly solution [2]. This method for the synthesis of liquid fuels involves the conversion of CO and H2 in syngas into both higher alcohols and hydrocarbons in the presence of a catalyst [3]. Nevertheless, owing to the higher costs of the FT process compared to other petrochemical technologies, the development of cost-effective catalysts plays an important role in reducing significant costs from industry [4]. The price of FT catalysts has directly affected both initial materials and production methods, as a whole [5]. More importantly, industries and specialists frequently use expensive bottom-up approaches and high-purity precursors for the preparation of traditional catalysts that can lead to an increase in the final price of products [6].

Catalyst supports and carriers, such as activated alumina, carbon, and zeolite, are an essential part of every catalyst, in addition to the promoter and active metal [7]. Therefore, to develop a low-cost catalyst, selecting an appropriate support is one of the most effective solutions [8]. Activated bauxite is a cost-effective alternative that can be reasonably considered due to its economic advantages [9,10].

The most prominent substances used in FT synthesis are the group VIII transition metals, including Ru, Fe, Ni, Co, Rh, and Pd. These metals are subject to ongoing research for FT synthesis and other related
catalytic reactions. However, Fe and Co are the most commonly used active metals in FTS catalysts due to their high activity and selectivity for the production of liquid hydrocarbons [11,12]. Iron is a commonly used active component in the synthesis of Fischer-Tropsch (FT) catalysts. This metal is often supported on a variety of materials, such as alumina or silica, to increase its surface area and optimize its performance. The resulting catalysts can be used to convert syngas into a variety of hydrocarbon products, such as diesel fuel and waxes. The higher alcohol synthesis (HAS) process uses a variety of catalysts based on the active metal involved. Copper-based binary and multiple catalysts like Cu-Zn have been investigated for the production of higher alcohols and oxygenates via HAS [13,14]. Among the early catalysts developed for higher alcohol synthesis, there are four main categories including (1) the modified methanol synthesis catalyst like Co, Fe, or Ni modified Cu/ZnO/α-Fe2O3 catalysts, (2) homogeneously mixed oxides containing mainly Co and Cu with small amounts of Zn, Zr, Al and alkali metals as modifiers, (3) the alkali modified Co-Mo catalyst, and (4) the Rh-based catalyst [15,16]. Molybdenum disulfide (MoS2) is a candidate for higher alcohol synthesis (HAS). However, the low activity of MoS2-based catalysts leads to comparatively low conversion of CO and subsequently low efficiency towards alcohols. To tackle this issue, a promoter like potassium is added to the catalyst. The addition of potassium has been found to enhance the activity of MoS2-based catalysts for higher alcohol synthesis [17,18].

There are three common (bottom-up) techniques for producing catalysts including: hydrothermal synthesis, co-precipitation, and wet-impregnation [19,20]. However, in these methods some parameters such as time, temperature, pH, and rotation speed of mixing must be controlled carefully [21–23]. Some precursors such as ammonium heptamolybdate (NH4)2Mo7O24, citric acid (C6H12O7), and thiourea (SC(NH2)2) can be used as the starting materials and the sulfur source for in situ synthesis of high-purity MoS2 under controlled conditions. As an alternative, in recent years, some researchers used synthetic molybdenite as a catalytic component and only carried out a series of activation processes [24,25]. Simeonov et al. [26] reported ball-milling for the activation of commercial high purity molybdenite (Aldrich) as the main material for the preparation of FT catalysts in the form of CoMoS/K without a carrier compound. Fedushchak et al. [27,28] obtained nanopowder catalysts based on synthetic molybdenite for the hydrodesulfurization (HDS) process by mechanical activation in the presence of dopants. Kouzu et al. [29] prepared microcrystalline MoS2 as an unsupported HDS catalyst using a mechanical milling process at a grinding speed of 2600 rpm during 10 hrs inside a neutral atmosphere.

According to the effect of copper on the activity and selectivity of hydrocarbons and oxygenates and its role in changing selectivity toward methane and other hydrocarbons which decreases the alcohol synthesis, a diminution of the copper content in the molybdenite is essential [30,31]. Many researchers have studied copper removal from molybdenite by a leaching process. Copper in the form of chalcopyrite (CuFeS2) is one of the most important impurities in molybdenite concentrates [32,33]. Padilla et al. [34] removed CuFeS2 from MoS2 by a sulfidation process with S2(g) followed by a leaching stage in dilute sulfuric acid media. Agaçayak et al. [35] investigated the effect of several parameters such as stirring speed, acid concentration, and temperature on chalcopyrite removal from molybdenite by leaching in nitric acid solution. Almeida et al. [36] studied the dissolution of chalcopyrite in acid solutions like nitric (HNO3), sulfuric (H2SO4), and hydrochloric (HCl) acids. The electrochemical impedance spectroscopy (EIS) and found that dissolution of chalcopyrite is controlled by diffusion. Also, Medvedev et al. [37] carried out a series of kinetic studies on leaching molybdenite concentrate by investigating the effect of temperature and nitric acid concentration. Typically, Benzešik et al. [38] worked on oxidizing the molybdenite concentrate by roasting experiments and evaluated the effect of different temperatures on leaching and copper removal with H2SO4 acid. Petrović et al. [39] investigated the leaching of chalcopyrite using hydrogen peroxide in hydrochloric acid media. Goodarzi et al. [40] investigated the parameters affecting the kinetics of molybdenite leaching including reaction time and temperature, H2O2 and H2SO4 concentration, pulp density, and rotation speed by optimization using the statistical Design of Experiments (DOE) technique. Leaching experiments were designed and analyzed by the Taguchi method. Shalchian et al. [41,42] addressed the effect of mechanical activation parameters on the leaching rate of molybdenite concentrate in nitric acid solution by ANOVA to determine the statistics of the main variations such as activation time, ball to powder ratio, rotation speed.

Basically, syngas molecules are chemically adsorbed on active sites of MoS2 which are found at rims and edges in the crystallites [43,44]. Therefore, the length and number of layers of MoS2 are effective parameters affecting the performance of catalysts, and these can be controlled by changing the catalyst preparation methods [45,46]. In the case of Mo-based catalysts, low-valence (Mo6+–2) and high-valence (Mo4+) species are responsible for HAS [47]. An increase in the interlayer spaces can facilitate the size reduction of particles using exfoliation processes that generate more catalytic sites [48,49]. For example, among the various exfoliation methods of MoS2 such as mechanical exfoliation, shear exfoliation, and solvent assisted exfoliation, the thickness of particles or the number of layers were observed to range between of 1–6, ~2–12, and multi-layers, respectively [50,51]. In spite of the mild conditions used for mechanical exfoliation as one of the most important factors, low production yield is still the main disadvantage. Gupta et al. [52] obtained stable aqueous dispersions of atomically-thin layered MoS2 nanosheets by an exfoliation process in a sonication bath in the presence of various ionic surfactants like cetyltrimethylammonium bromide (CTAB), and sodium dodecyl sulfate (SDS). Simeonov et al. [26] found that ball-milled samples showed a size reduction, and subsequently, the enhancement of specific surface area. However, agglomeration phenomena happened through further milling for 4 weeks. Hoseinpour et al. [53] addressed the influence of alumina powders on structural changes of MoS2 during a ball-milling process at 315 rpm and a ball-to-powder mass ratio of 41 over various times up to 12 hrs. They observed that at the beginning, layers of molybdenite started to slide and separate from each other and the presence of alumina acted as a positive agent for the size reduction of particles. Wafa et al. [54] carried out the mechanical milling procedure on synthesized MoS2 at 3000 rpm for different time intervals between 1 and 50 hrs which could significantly decrease average crystallite sizes of MoS2 up to 3 nm.

This study focused on the design and production of four different types of K2CO3-Molybdenite catalysts supported on mesoporous activated bauxite. These catalysts were created using a top-down approach and inexpensive mineral resources. The researchers then evaluated the catalytic performance of these catalysts in higher alcohol synthesis (HAS) and hydrocarbon synthesis from syngas using a fixed-bed reactor. Additionally, the study investigated the impact of activation processes, specifically HNO3 leaching and dry ball-milling of low-grade molybdenite, on alcohol selectivity, CO conversion in HA and FT synthesis.

2. Experimental

2.1. Materials

A sample of raw molybdenite concentrate (RMC) that is known as low-grade ore containing <5% molybdenum was supplied from the Sarcheshmeh Copper Complex mine in the Kerman province of Iran. Ethyl acetate and nitric acid 65% (HNO3) were purchased from Sigma-Aldrich while polyethylene glycol (PEG) (MW = 400) was procured from the Shazand Petrochemical Company of Iran. Table 1 shows the chemical composition of RMC as determined by the ICP-MS method. Table 2 presents the analyses of the raw bauxite (RB) and the mesoporous activated bauxite (MAB) used as catalyst support material with specific surface area of 131.07 m2/g as prepared according to previous reports for designed HAS catalysts.
3.2. Washing and leaching process

In order to eliminate copper from molybdenite concentrate, scientists have explored various methods, with a focus on chalcopyrite as the primary impurity. These techniques include sulfidation, leaching with nitric and sulfuric acid, as well as conducting kinetic studies on molybdenite leaching. The studies have also examined the impact of different factors on the dissolution and removal of chalcopyrite, such as stirring speed, acid concentration, and temperature. Electrochemical impedance spectroscopy was utilized to investigate the dissolution of chalcopyrite in solutions containing nitric, sulfuric, and hydrochloric acids. The results revealed that diffusion plays a significant role in the dissolution process. Furthermore, kinetic studies were conducted to assess how the concentration of nitric acid and temperature affect the leaching of molybdenite concentrate. Some researchers have directed their efforts towards removing copper from molybdenite concentrate by oxidizing molybdenite through roasting experiments. Additionally, another study focused on leaching chalcopyrite using hydrogen peroxide in hydrochloric acid. The researchers employed the statistical Design of Experiments method to optimize and investigate the key parameters that influence molybdenite leaching. The Taguchi method was utilized to design and analyze the leaching experiments. Furthermore, a scientist examined how variations in mechanical activation parameters, such as activation time, ball-to-powder ratio, and rotation speed, can impact the examined how variations in mechanical activation parameters, such as design and analyze the leaching experiments. Furthermore, a scientist in order to produce extremely thin MoS$_2$ nanosheets at the atomic level. While mechanical peeling has shown promise, its low yield remains a significant drawback. Additionally, it has been discovered that ball-milled samples are more effective in reducing size and enhancing specific surfaces. Alumina powder has also been identified as a beneficial agent in reducing particle size during the ball milling process.

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Mo</th>
<th>S</th>
<th>Cu</th>
<th>Fe</th>
<th>Others</th>
</tr>
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<tbody>
<tr>
<td>%</td>
<td>52.38</td>
<td>35.01</td>
<td>2.45</td>
<td>4.13</td>
<td>6.03</td>
</tr>
</tbody>
</table>

2.4. Coating and forming catalysts

In order to achieve adequate coverage of catalytic particles on the surface of the substrate, a combination of molybdenite concentrate and activated bauxite was introduced into a jar-mill device. The potassium carbonate/catalyst powder/support mass ratio (K$_2$CO$_3$/IMC or PMC/MAB) was maintained at 1/2/4 for all samples. The milling process took place under ambient atmospheric conditions with a rotation speed of 70 rpm for a duration of 12 hrs. Subsequently, a catalyst paste was prepared by blending bentonite powder, PEG, and distilled water. These ingredients served as a mineral binder, organic binder, and moisture agent, respectively. The resulting catalyst paste was then shaped into extruded cylinders with an outer diameter of 2 mm and a length ranging from 2 to 4 mm, forming cylindrical cross-sections. Finally, all samples underwent calcination at a uniform temperature of 350 °C for a duration of 4 hrs.

2.5. Characterization of catalysts

The BelSorp mini II Brunauer-Emmett-Teller (BET) analyzer was utilized to estimate the specific surface area, pore size, and pore volume distribution of all samples. To eliminate any moisture present in the samples, they were initially dried at 120 °C for 2 hrs using the BelPrep VAC II instrument. Subsequently, nitrogen gas was injected at 77 K to measure the specific surface area and average pore diameter. For the analysis of sample morphology, the SEM proX model with a voltage of 15 kV was employed. Elemental mapping and quantification were performed using the MIRA II energy-dispersive X-ray spectroscopy (EDS) analyzer, which has a maximum energy resolution of 129 eV. In this study, the catalytic powder specimens were securely mounted onto the sample holder using a non-conductive and vacuum-stable adhesive or double-sided tape. Elemental and chemical analysis of the samples were conducted using a Spectro xepos50 spectrometer for X-ray fluorescence (XRF) measurements. The metal content was determined using a high-resolution inductively coupled plasma-mass spectrometer (ICP-MS, Thermo Scientific ELEMENT 2XR). To measure the average particle size (Zavg) and size distribution profile of the molybdenite particles after undergoing chemical–mechanical treatment, Dynamic Light Scattering (DLS) was employed. The measurements were performed using a Horiba model SZ100 DLS analyzer with a count rate of 1585 kCPS and a dispersion medium viscosity of 0.896 mPa.s. The analysis was conducted at a holder temperature of 25 °C.

2.6. Catalytic reaction tests

The chemical process is characterized by the adsorption of syngas molecules on active sites found at the edges and rims of MoS$_2$ crystals. In order to enhance the performance of the catalyst, it is necessary to effectively control the length and number of MoS$_2$ layers, which can be achieved by adjusting the methods used for catalyst preparation. In the case of Mo-based catalysts, the HAS process is influenced by both low-valence and high-valence species. By increasing the spaces between layers, the exfoliation process can result in smaller particle sizes and the creation of more catalytic sites.

In this study, the fixed-bed reactor at the Research Institute of Petroleum Industry (RIP1) in Iran was utilized to evaluate 2 gr catalyst under specific conditions. The reactor was operated at a temperature of...
360 °C and a pressure of 20 bar, with a syngas feed having a H₂/CO stoichiometric ratio of 2 and a gas hourly space velocity (GHSV) of 1500 h⁻¹. The tests were conducted at a steady state after 24 hrs of reaction time, with stability and activity studies performed between 12 and 48 hrs. To ensure accuracy, the reactor output was measured and averaged over three repetitions. The liquid products, including alcohols and water, were analyzed using gas chromatography (GC) with Porapak-Q columns and TCD and FID detectors. The gaseous products were analyzed using a gas chromatograph with an alumina-isolated column and TCD and FID detectors. Methane and methanol were used as reference compounds for correlating the gas and liquid phase products, respectively. The conversion (XCO) was calculated based on the molar flow rates of carbon monoxide (CO) entering (FCOin) and exiting (FCOout) the reactor, as shown in Equation (1) [55].

$$X_{CO} = \frac{F_{COin} - F_{COout}}{F_{COin}} \times 100$$  \hspace{1cm} (1)

The selectivity of component 'i' (Sₖ) was calculated by dividing the molar flow rate of the component Fᵢᵢ out to the amount of carbon monoxide converted to the reaction products (Equation (2) [55].

$$S_i = \frac{F_{i_{out}}}{F_{COin} \times 100} \times 100$$  \hspace{1cm} (2)

3. Results and discussion

Fig. 1 illustrates the EDS analysis of molybdenite before and after undergoing chemical leaching for purification. The catalytic behavior of molybdenite in the alcohol synthesis process for FT was influenced by the presence or absence of copper, as shown in Fig. 1(a). Based on the initial chemical composition of the concentrate, the primary objective of the leaching process was to remove CuFeS₂, which is known to be one of the significant impurities in the ore [56]. After conducting ICP-MS analysis on the filtered molybdenite following the leaching process, it was determined that the removal efficiency of copper was 95.75%. Fig. 1(b) demonstrates the outcome of the EDS analysis on the purified MoS₂ concentrate (PMC) under operational conditions, confirming the enhanced purity of molybdenum and successful removal of copper.

Strong covalent bonds are present between one Mo and two S atoms within MoS₂ layers, while MoS₂ monolayers are connected by weak van der Waals forces [57]. Unsupported MoS₂ monolayers as catalysts have certain limitations, such as a low rate of production, low porosity, and a
significant level of aggregation, which ultimately result in reduced catalytic activity [58,59]. In contrast, catalysts based on multilayer-MoS₂ possess an expanded active surface area and exhibit greater activity [60]. Therefore, it is anticipated that few-layer structured and supported MoS₂ catalysts will exhibit excellent efficiency in heterogeneous catalysis across a wide range of reaction systems. SEM images of the washed impure MoS₂ (IMC) clearly demonstrate the presence of particles with multiple layers, as depicted in Fig. 2(a). Following the leaching process, an expansion in the inter-layer spacing was observed in the treated MoS₂, as shown in Fig. 2(b), which can be attributed to the occurrence of wet chemical etching [61]. One of probable reason of this lattice expansion between layers of MoS₂ may be the removal of NOₓ [33]. According to literature review, polyethylene glycol provides some properties including the enhancement of the catalytic activity of MoS₂ owing to the functionalization phenomena [62,63], creation of adhesion between catalytic particles and substrate and improvement of plasticizer features [64,65] in the next steps.

The Dow Chemical Company and Clarion discovered a method that was used in this study to activate commercially available molybdenum sulfide as a catalyst precursor [26]. Mechanical exfoliation was performed by dry milling which not only acted as an effective procedure to produce submicron particles [66], but also affected the catalytic activity [67]. The size changes that occurred during the dry-mechanical milling process were monitored using SEM images. Fig. 2(c) clearly shows that the flakes have significantly reduced in size compared to the initial materials shown in Fig. 2(a), which can be attributed to the 36-hr ball-milling process. Furthermore, when comparing images at the same magnification, a noticeable reduction in the size of MoS₂ particles was observed.

The size distribution of particles in exfoliated molybdenite powder samples, both impure and purified, in the sub-micron range, was measured using the Dynamic Light Scattering (DLS) technique, as depicted in Fig. 3. Through the Z-average value and the polydispersity (PI) index, information regarding the width of the size distribution and the uniformity of particle distribution within the sample was obtained. This analysis specifically aimed at extracting size-related information of particles (eIMC and ePMC) using a light beam (electromagnetic wave). In this study, the eIMC catalytic powder exhibits a higher PI index of 0.802, whereas the ePMC catalytic powder has a PI index of 0.606. These values indicate that the samples are somewhat polydisperse, suggesting a wide distribution of particle sizes. A PI value ≤ 0.1 is considered highly monodisperse, while values between 0.1 and 0.4 indicate moderate polydispersity, and values exceeding 0.4 indicate high polydispersity [68].

The Z-average of the ePMC catalytic powder is measured to be 438.7, while the eIMC catalytic powder exhibits a higher Z-average of 1018.3. This indicates that the majority of particles in the ePMC powder have a hydrodynamic radius of approximately 438 nm, which is smaller compared to the particles in the eIMC powder.

The particle diameter represents the size of the particles in molybdenite after a 36-hour exfoliation process using dry-mechanical milling. The effect of chemical activation as a pre-treatment is observed in enhancing the distance between MoS₂ layers in the ePMC catalytic powder (Fig. 2(b)), compared to the initial MoS₂ layers (Fig. 2(a)). This chemical activation, followed by facilitating particle size reduction, results in a smaller particle diameter of 261.5 nm for the ePMC catalytic powder. On the other hand, the eIMC powder, which is not chemically activated, exhibits a larger particle diameter of 816.1 nm. These findings indicate that the ePMC powder has a broader size distribution, larger hydrodynamic size (Z-average), and larger particle diameter compared to the eIMC catalytic powder [68]. As a result, Fig. 3 shows that the particle size of ePMC was reduced more significantly through low-energy mechanical exfoliation using milling compared to IMC.

Fig. 4 displays the porous characteristics and pore size analysis of HAS catalysts. The N₂ adsorption–desorption isotherm curves for all the developed HAS catalysts supported on the catalytic carrier (MAB) are also depicted in Fig. 4. It can be observed that all the catalysts exhibit a characteristic irreversible type IV isotherm with distinct H2(ii) hysteresis loops [10]. Hysteresis of type H2(ii) occurs when the curve shape represents a narrow distribution of body pores with a wide range of neck sizes. Additionally, the hysteresis loop observed in HAS catalysts was seen at relative pressures (P/P₀) ranging from 0.4 to 1.0, which is a dimensionless parameter. Generally, mesoporous materials exhibit Type IV isotherms. The filling of mesopores occurs through a different mechanism, involving the formation of multiple layers followed by capillary condensation. This mechanism results in Type IV(a) or Type IV(b) isotherms, depending on the size of the mesopores. In Type IV(a) isotherms, hysteresis occurs due to capillary condensation in larger mesopores (greater than 4 nm), and there is a correlation between the shape of the observed hysteresis loop and the textural properties of the catalyst [9,10,69].

Table 3 compares the texture properties of the K-MoS₂ catalyst with varying levels of purity. Fig. 4 displays the nitrogen adsorption–desorption isotherms of the catalysts. Among these HAS catalysts, K-ePMC-MAB exhibited the highest specific surface area, pore diameter, and pore volume, while K-IMC-MAB had the lowest values. This suggests that the textural properties of the catalysts were significantly influenced by the chemical–mechanical activation method. Generally, smaller particle sizes and larger specific surface areas are advantageous for exposing more corners and defects, which is beneficial for the catalytic conversion of syngas [18].

In order to assess the effectiveness of coating catalytic and alkali promoter particles on the substrate, the powdered sulfide catalyst underwent EDS analysis and elemental mapping. Fig. 5 presents the results...
of the EDS analysis conducted on the K-PMC-MAB catalyst powder supported on Mesoporous activated bauxite. The analysis confirms the presence of molybdenum as the active metal, along with oxygen and carbon as the primary components of PEG. Additionally, the EDS profiles indicate the relative amounts of aluminum, silicon, titanium, and iron, which are constituents of the activated bauxite substrate (Fig. 5(a)).

Moreover, the elemental mapping reveals a uniform distribution of potassium carbonate, serving as an alkali promoter to enhance alcohol synthesis (Fig. 5(b)). The presence of potassium is crucial as, without its addition, the CO conversion is minimal and the selectivity to C-OH is high, resulting in a negligible selectivity to C$_3$+ alcohol. Previous studies have shown that the addition of K$_2$CO$_3$, KOH, or CH$_3$COOK to MoS$_2$ can...
increase the selectivity to alcohol by up to 30–35% [70].

By examining the chemical composition of the catalyst powder during the preparation process, it becomes evident that the K-PMC-MAB catalyst exhibited a well-dispersed distribution of K, Mo, and S elements. Notably, a significant amount of Mo and S content was observed on the surface of the mesoporous activated bauxite (Fig. 5(b)). In the case of the K-PMC-MAB catalyst, the distribution ratio of C, which represents the polyethylene glycol binder, as well as the Fe and Ti elements, which are secondary components of the MAB substrate, were lower compared to the main composition of the catalyst (Fig. 5(a)).

Fig. 5 demonstrates the use of EDS analysis for elemental mapping, which is a qualitative technique utilized to study the dispersion of catalytic material on a substrate. Through the mapping of element distribution on the surface of the substrate, this technique offers valuable insights into the effectiveness of the dispersion process and the subsequent catalyst performance.

The CO hydrogenation reaction was conducted under similar conditions (360 °C, 20 bar, 1500/h, and H$_2$ to CO molar ratio of 2) over K-

<table>
<thead>
<tr>
<th>Samples</th>
<th>S$_\text{BET}$ (m$^2$/g)</th>
<th>Average Pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-IMC-MAB</td>
<td>36</td>
<td>16</td>
<td>0.15</td>
</tr>
<tr>
<td>K-PMC-MAB</td>
<td>52</td>
<td>12</td>
<td>0.16</td>
</tr>
<tr>
<td>K-ePMC-MAB</td>
<td>72</td>
<td>10</td>
<td>0.17</td>
</tr>
<tr>
<td>K-eIMC-MAB</td>
<td>63</td>
<td>14</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 3
Surface area and average pore size of the HAS catalyst samples.

![Graph](image)

Fig. 5. Results of EDS analysis of K-PMC-MAB catalyst powder.
promoted molybdenite-based catalysts supported on mesoporous activated bauxite. The conversion and selectivity results obtained from this reaction are presented in Table 3 and Fig. 6. The liquid products were collected, and the exit gas was analyzed to determine the CO conversion. The analysis of the liquid products revealed that the major products were methanol and ethanol, along with side products such as hydrocarbons. Undesirable byproducts like methane and CO2 were also observed. The results demonstrate the impact of Cu reduction in the form of chalcopyrite and mechanical activation through dry-ball milling on the catalytic properties for synthesizing higher alcohols from synthesis gas, following an initial induction period of 24 h. In Table 3 and Fig. 6, the term “higher alcohols” refers to ethanol and alcohols with a carbon number greater than 2 (C2, alcohols).

On the other hand, the activity and selectivity of the catalyst were influenced by the removal of a portion of its surface through treatment with nitric acid. This chemical activation process resulted in the decline of copper, sulfur, and iron from the catalytic molybdenite surface, subsequently enhancing the catalyst’s performance. The findings indicate that the selectivity towards C2, alcohols increased significantly (more than 95%) when the copper content in the form of CuFeS2 was reduced in the molybdenite-based HAS catalyst (K-IMC- and K-ePMC-MAB) compared to the un-leached or impure catalysts (K-IMC- and K-ePMC-MAB).

Based on these findings, the purification of molybdenite through nitric acid leaching and the reduction of chalcopyrite content had a notable impact on increasing the alcohol selectivity of K-ePMC-MAB compared to K-eIMC-MAB. The selectivity increased from 49.8% to 52.3%. Comparing runs 1 and 2 with runs 3 and 4 reveals that the exfoliation technique acted as a mechanical activation method. Consequently, the size reduction of molybdenite particles during dry milling (or mechanical exfoliation) appears to have led to an improvement in activity. It is worth noting that the total mass balance, as well as the carbon, hydrogen, and oxygen elemental mass balances, were calculated and found to be within the range of 100 ± 5%.

The main process involved in higher alcohol synthesis is the hydrogenation of CO and/or CO2 using a catalyst, as described in Equation (3). This synthesis typically follows several steps. Firstly, the metal catalyst reacts with CO and/or CO2 to form metal carbonyl complexes. These complexes then dissociate into metal atoms and CO, with this dissociation often being the rate-determining step. Next, the metal atoms react with H2 to form metal hydrides, which subsequently react with carbon monoxide to produce alcohols. The alcohols generated undergo chain growth reactions, resulting in the formation of higher alcohols. Additionally, secondary reactions may occur, such as dehydration or hydrogenation, which can lead to the formation of other compounds.

\[
2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \tag{3}
\]

The results of fixed-bed reactor tests on K-promoted molybdenite catalysts supported on mesoporous activated bauxite are shown in Table 4.

<table>
<thead>
<tr>
<th>Sample K/Mo/Ba ratio:</th>
<th>Selectivity (%)</th>
<th>Alcohol</th>
<th>C2H5OH</th>
<th>C3H7OH</th>
<th>C2, alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2/4</td>
<td></td>
<td>Alcohol</td>
<td>C2H5OH</td>
<td>C3H7OH</td>
<td>C2, alcohol</td>
</tr>
<tr>
<td>K-IMC-MAB</td>
<td>41.5</td>
<td>15.6</td>
<td>17.6</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>K2CO3·MoS2 (impure) / mesoporous activated bauxite (SBA-131)</td>
<td>43.1</td>
<td>17.1</td>
<td>15.4</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>K-PMC-MAB</td>
<td>49.8</td>
<td>17.6</td>
<td>20.7</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td>K2CO3·MoS2 (purified) / mesoporous activated bauxite (SBA-131)</td>
<td>52.3</td>
<td>19.1</td>
<td>21.1</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>K-ePMC-MAB</td>
<td>43.1</td>
<td>17.1</td>
<td>15.4</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>K2CO3·MoS2 (impure-exfoliated) / mesoporous activated bauxite (SBA-131)</td>
<td>49.8</td>
<td>17.6</td>
<td>20.7</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td>K-ePMC-MAB</td>
<td>52.3</td>
<td>19.1</td>
<td>21.1</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>K2CO3·MoS2 (purified-exfoliated) / mesoporous activated bauxite (SBA-131)</td>
<td>52.3</td>
<td>19.1</td>
<td>21.1</td>
<td>12.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. These tests were conducted with the same operating conditions, maintaining a constant flow of inlet reactants and outlet synthetic products. The data in Table 5 demonstrate the effectiveness of developed low-cost catalysts in driving the desired reactions and producing the targeted (alcohol and higher alcohol) synthetic products. The table provided a comprehensive overview of the test results, including the composition of the inlet syngas (CO and H2) and the resulting outlet products (alcohols and CO2).

In terms of the production of total alcohol (CH3OH + C2H5OH + C3H7OH + C2, alcohol), the catalysts exhibit varying levels of performance. K-IMC showed the lowest total alcohol production amount of 0.0031 mol/hr, while K-ePMC showed the highest amount of 0.0058 mol/hr. This suggests that K-ePMC is the most effective catalyst for the synthesis of total alcohols among the four catalysts tested.

Additionally, the use of mechanical exfoliation as an activation process has demonstrated a positive effect on reducing the particle size and increasing the activity of molybdenite-based catalysts for HAS. The smaller particle size of exfoliated MoS2 has resulted in a higher number of active sites available for catalytic reactions, thereby improving both catalytic activity and selectivity. Moreover, mechanical exfoliation has the ability to introduce defects and edge sites in MoS2, which can further enhance catalytic activity and selectivity for HAS. These defects and edge sites serve as active sites for the reduction of CO to alcohols and higher alcohols, offering higher reaction rates and improved selectivity.

The main reason for the above reaction results might be ascribed to the distinct differences in the particle size of the active compounds. Based on the SEM and DLS results, it was observed that the K-ePMC-MAB catalyst had a smaller catalytic particle size (ePMC: 261.5 nm) on the substrate and exhibited the largest specific surface area (72 m2/g) compared to the eIMC powder with the particle size of 816.1 nm that supported on Mesoporous activated bauxite (wSBA: 63 m2/g). This suggests that the K-ePMC-MAB catalyst contained smaller few-layered particles which were well-dispersed on the substrate in comparison to the K-eIMC-MAB catalyst. Combined with the catalytic performance shown in Fig. 6, it is speculated that the smaller catalyst particle with a higher dispersion facilitated CO conversion and C2, alcohol selectivity. The dispersion of the catalytic material is an important parameter that can affect the catalytic activity and selectivity of the material. In this work, Elemental mapping via EDS analysis is an effective technique for studying the dispersion of K2CO3 and PMC on MB. By mapping the spatial distribution of elements, including catalytic materials, on the activated bauxite’s surface, elemental mapping provided useful information into the effectiveness of the dispersion process and the performance of the resulting catalyst.

Ferrari et al. [71] found that smaller particles of MoS2 had a positive effect in the C2, OH selectivity in HAS, which is consistent with obtained results in their work. Simeonov et al. [26] shown that when Aldrich (high purity) MoS2 is not ball-milled, only about 2.5% CO conversion is obtained, while in the present study, CO conversion reached 33.1% with chemical activation without any mechanical milling. While 39.2% CO conversion was achieved by only mechanical activation of the catalyst.

The alcohol distribution over the four catalysts is shown in Table 4. The amount of alcohol products obtained over the K-IMC-MAB, K-PMC-MAB, K-ePMC-MAB and K-ePMC-MAB catalysts increased in the order of C2H5OH > CH3OH > C3H7OH > C2, alcohol. Furthermore, it indicates that the K-ePMC-MAB catalyst had a better carbon chain growth ability with respect to higher alcohol formation. Andersson et al. [72] suggested that the increase in CO conversion also led to the formation of long-chain alcohols, which agrees with the present results.

Table 6 summarizes the performance of molybdenite-based catalysts supported on mesoporous activated bauxite, prepared using a top-down approach involving leaching and dry ball-milling method. These results are compared to catalysts reported in the literature that were prepared using conventional (bottom-up) methods. Conventional Mo-based catalysts with various additives such as alkali metals (K), Co, Ni, and Rh are commonly used for alcohol synthesis. As shown in Table 6, these
catalysts generally exhibit either high selectivity towards alcohol (greater than 90%) but low CO conversion (<15%), or relatively high CO conversion (<45%) but low selectivity to alcohol (<50%). Among the catalysts developed in this study, the one with a K/Mo ratio of 0.5/1 demonstrated the best performance, even at a relatively low pressure of 20 bar. It achieved the CO conversion of 41.9% and the selectivity of 52.3% towards alcohol. The K-Mo-MAB catalysts exhibited significantly acceptable CO conversion compared to metal-promoted catalysts, suggesting that the presence of Ni, Co, or Rh as promoters on MoS$_2$ sites is unnecessary to enhance the catalyst’s performance under the studied experimental conditions. Chemically activated catalysts, specifically K-PMC-MAB and K-ePMC-MAB, demonstrated excellent CO conversion rates and selectivity towards alcohols. Conversely, K-IMC-MAB and K-eIMC-MAB, which contained impurities, had a detrimental effect on the reaction, resulting in higher levels of C$_2$+OH. Finding two case studies with identical operating conditions is certainly challenging. However, the main objective of this research was to create cost-effective catalysts and implement energy-efficient practices within specific operating conditions. Therefore, the results obtained from the developed catalysts have attracted attention in research due to their ability to perform equally well or even better under equal or lower operating conditions compared to those reported in the literature. The performance of cost-effective mineral-based catalysts has surpassed that of expensive synthetic catalysts that require higher operating conditions. However, it is a widely acknowledged scientific fact that higher operating parameters such as temperature, H$_2$/CO ratio, GHSV, and pressure generally lead to improved catalyst performance, conversion, efficiency, selectivity, and other factors. Nevertheless, it is important to consider that higher energy consumption associated with these parameters will result in increased costs. It is worth mentioning that the catalysts mentioned in the literature typically contain at least one metallic promoter, which enhances their performance. In contrast, molybdenite-based catalysts have demonstrated impressive results despite not containing any metallic promoter.

Both non-exfoliated catalysts, K-PMC-MAB and K-IMC-MAB, exhibited comparable selectivity and activity, with satisfactory levels of C$_2$, alcohol selectivity and minimal hydrocarbon production. Additionally, the exfoliated catalysts demonstrated similar selectivity and activity, but with even higher C$_2$ alcohol selectivity and lower hydrocarbon formation compared to the two non-exfoliated samples.

In contrast to the findings of Zhang et al. [80], this research demonstrates that the presence of iron, specifically in the form of pyrite impurity in HAS catalyst compositions, can actually lead to catalyst deactivation. Surprisingly, the presence or absence of copper in the form of CuFeS$_2$ has no impact on the deactivation rate of the catalyst. During the catalytic reaction, sulfur from pyrite can react with the active species of the catalyst, resulting in the formation of volatile sulfur compounds. These compounds can then block the active sites of the catalyst, reducing its catalytic activity. Additionally, the presence of pyrite can lead to the formation of iron sulfide, which can accumulate on the surface of the catalyst and create diffusion blockages, thereby decreasing the active surface area of the catalyst. Furthermore, the

Table 5

<table>
<thead>
<tr>
<th>Num</th>
<th>Catalyst Name</th>
<th>Reactor Outlet (mol/hr)</th>
<th>CH$_3$OH</th>
<th>C$_3$H$_5$OH</th>
<th>C$_2$, alcohol</th>
<th>Carbon outlet (gr/hr)</th>
<th>CO outlet</th>
<th>CO$_2$ outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K-IMC-MAB</td>
<td>0.0018</td>
<td>0.0010</td>
<td>0.0003</td>
<td>0.50</td>
<td>0.03</td>
<td>0.0031</td>
<td></td>
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<tr>
<td>2</td>
<td>K-PMC-MAB</td>
<td>0.0024</td>
<td>0.0011</td>
<td>0.0004</td>
<td>0.49</td>
<td>0.03</td>
<td>0.0033</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>K-eIMC-MAB</td>
<td>0.0029</td>
<td>0.0017</td>
<td>0.0005</td>
<td>0.49</td>
<td>0.03</td>
<td>0.0038</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>K-ePMC-MAB</td>
<td>0.0034</td>
<td>0.0019</td>
<td>0.0005</td>
<td>0.49</td>
<td>0.002</td>
<td>0.0040</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6. Catalytic performance of extrudate K$_2$CO$_3$-MoS$_2$ catalysts supported on mesoporous activated bauxite prepared with the top-down approach. Reaction conditions: GHSV = 1500/h, T = 360 °C, P = 20 bar, H$_2$/CO ratio = 2.
presence of pyrite can also contribute to the formation of other sulfur-containing species, such as thioacetamide, which further contributes to the deactivation of the catalyst.

Furthermore, sulfur in the form of MoS₂ can serve as a catalyst promoter, facilitating the generation of oxygen-containing intermediates. These intermediates can subsequently undergo additional reactions to produce higher alcohols. Additionally, the presence of this particular form of sulfur can hinder the formation of undesirable by-products like olefins, which could otherwise diminish the selectivity of the catalyst [80].

The active sites of K₂CO₃-molybdenite-based HAS catalysts are the metallic molybdenum particles located on the surface of the MAB. These particles play a crucial role in providing active sites for the adsorption of reactant molecules, thereby facilitating the formation of alcohol and higher alcohol compounds. These catalysts have demonstrated notable activity in the synthesis of long-chain alcohols during the Higher Alcohol Synthesis process. It is believed that the active sites present in these catalysts promote the adsorption and activation of reactant molecules, leading to the desired reaction outcomes.

### 4. Conclusions and future outlook

In this study, affordable molybdenite-based catalysts supported on mesoporous active bauxite were developed using a top-down approach for alcohol synthesis via the HAS process. The investigation focused on the chemical composition of low-grade molybdenite concentrate, particularly the presence of chalcopyrite as the main impurity, and the preparation process involving chemical purification and mechanical exfoliation. It was observed that leaching with nitric acid and subsequent removal of chalcopyrite from molybdenite enhanced alcohol synthesis using this HAS catalyst. The exfoliation process led to the formation of nanoscale molybdenite particles through dry exfoliation. This work

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### Table 6
Comparison of the CO conversion and alcohol selectivity between developed catalysts in this work and the catalysts reported in the literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method*</th>
<th>CO conversion (%)</th>
<th>Alcohol selectivity (%)</th>
<th>Higher alcohol selectivity (%)</th>
<th>Operating conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-eIMC-MAB</td>
<td>top-down approach</td>
<td>39.2</td>
<td>49.8</td>
<td>32.2</td>
<td>T: 360 °C</td>
<td>This work</td>
</tr>
<tr>
<td>K-ePC-MAB</td>
<td></td>
<td>41.9</td>
<td>52.3</td>
<td>33.2</td>
<td>GHSV: 1500/h</td>
<td></td>
</tr>
<tr>
<td>K-IMC-MAB</td>
<td></td>
<td>27.6</td>
<td>42.1</td>
<td>26.5</td>
<td>H₂/CO: 2</td>
<td></td>
</tr>
<tr>
<td>K-PMC-MAB</td>
<td></td>
<td>33.1</td>
<td>43.1</td>
<td>26</td>
<td>P: 20 bar</td>
<td></td>
</tr>
<tr>
<td>K-Co-Mo (unsupported)</td>
<td>bottom-up approach</td>
<td>12.5–48</td>
<td>Not reported</td>
<td>32–71</td>
<td>T: 360–340 °C</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GHSV: 2000/h</td>
<td></td>
</tr>
<tr>
<td>K-Co-Mo (unsupported)</td>
<td>top-down approach</td>
<td>2–27.5</td>
<td>Not reported</td>
<td>33–49</td>
<td>T: 330–340 °C</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂/CO: 2</td>
<td></td>
</tr>
<tr>
<td>K-Co-Mo (unsupported)</td>
<td>bottom-up approach</td>
<td>8.7–28</td>
<td>37.7–47.9</td>
<td>15.4–57.5</td>
<td>T: 300 °C</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GHSV: not mentioned</td>
<td></td>
</tr>
<tr>
<td>K-Ni-Mo-MgAl</td>
<td>bottom-up approach</td>
<td>5.1–9.5</td>
<td>23.3–59.9</td>
<td>23.3–49.4</td>
<td>T: 350 °C</td>
<td>[3]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>GHSV: 3200/h</td>
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</tr>
<tr>
<td>K-Co-Mo</td>
<td>bottom-up approach</td>
<td>35.7–58.1</td>
<td>Not reported</td>
<td>34.4–66.3</td>
<td>T: 300 °C</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂/CO: 1</td>
<td></td>
</tr>
<tr>
<td>K-Co-Mo-MWCNTs</td>
<td>bottom-up approach</td>
<td>29.1</td>
<td>29.3</td>
<td>13.8</td>
<td>T: 305–325 °C</td>
<td>[74]</td>
</tr>
<tr>
<td>K-Co-Mo-MWCNTs</td>
<td></td>
<td>46.9</td>
<td>55.6</td>
<td>30.6</td>
<td>GHSV: 1225/h</td>
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<tr>
<td></td>
<td></td>
<td>47.3</td>
<td>56.5</td>
<td>30.9</td>
<td>H₂/CO: 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>51.2</td>
<td>71.8</td>
<td>39.4</td>
<td>P: 75 bar</td>
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<tr>
<td>K-Co-Rh-Mo-MWCNTs</td>
<td></td>
<td>35.6</td>
<td>48.5</td>
<td>22.8</td>
<td>T: 301–370 °C</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GHSV: 3000–10000/h</td>
<td></td>
</tr>
<tr>
<td>K-Co-Rh-Mo-MWCNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂/CO: 0.5–3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>P: 55–89 bar</td>
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</tr>
<tr>
<td>K-Co-Rh-Mo-MWCNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T: 340–360 °C</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GHSV: 4500/h</td>
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<tr>
<td>K-Co-Rh-Mo-MWCNTs</td>
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<td></td>
<td></td>
<td></td>
<td>H₂/CO: 1–1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>P: 87–117 bar</td>
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</tr>
<tr>
<td>K-Co-Rh-Mo-MWCNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T: 240–300 °C</td>
<td>[77]</td>
</tr>
<tr>
<td>K-Co-Mo-Zeolite</td>
<td>bottom-up approach</td>
<td>2.29–22.7</td>
<td>–</td>
<td>23.7–61.1</td>
<td>T: 270 °C</td>
<td>[78]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>GHSV: 3000–9000/h</td>
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<tr>
<td>K-Co-Mo-Zeolite Monolith</td>
<td>bottom-up approach</td>
<td>35</td>
<td>64</td>
<td>29</td>
<td>H₂/CO: 2</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** *The top-down approach refers to utilize the bulk materials and change them into smaller particles around nanoscale. The bottom-up approach refers to nanostructures are synthesized onto the substrate by stacking atoms onto each other, which gives rise to crystal planes, crystal planes further stack onto each other, resulting in the synthesis of the nanostructures [79]."
(e)PMC-MAB catalysts, resulting from the leaching process, did not have an impact on their deactivation rate. However, the presence of iron, even after leaching, as an impurity (such as pyrite) in the composition of HAS catalysts could be the sole reason for their deactivation. Overall, the most effective method for developing cost-effective mineral-based catalysts for alcohol synthesis involves leaching followed by dry milling as a chemical–mechanical activation procedure. Additionally, mesoporous activated bauxite, leached molybdenite concentrate, and PEG can be utilized as a catalytic carrier, active metal, and organic binder, respectively, in the development of HAS catalysts.

The research introduces an innovative approach to creating catalysts by utilizing K₂CO₃-molybdenite and activated bauxite. This method emphasizes the chemical–mechanical activation of molybdenite as a cost-effective alternative to traditional precursors. The newly developed catalysts have demonstrated impressive performance when compared to existing synthetic types. As a result, the research recommends that other scientists conduct supplementary characterization tests on mineral-based catalysts developed using a similar approach. These tests, such as TPR, XRD, XPS, TEM, etc., can provide valuable insights into the properties and effectiveness of the catalysts. Furthermore, the research highlights several areas for further exploration, including catalyst design, co-feeding of promoters, catalyst regeneration, catalyst poisoning, alternative catalysts, modification of MoS₂ structure, optimization of preparation method, and understanding mechanisms of catalyst deactivation.

Data availability

Data will be made available on request.

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References


