



A novel approach of methane dehydroaromatization using group VIB metals (Cr, Mo, W) supported on sulfated zirconia

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Abstract

Methane dehydroaromatization (MDHA) is a direct activation approach to convert methane to value-added chemicals in a single step. This requires no intermediate step, making it a commercially economic approach. Mo supported on HZSM-5/MCM-22 is a well-studied catalyst for this reaction, where Mo sites are responsible for activating methane to C₂H_y dimers, which can oligomerize on HZSM-5 Bronsted acid sites to produce aromatics. Challenges for these bifunctional catalysts involve rapid coking and low product yield. In this study, a novel catalytic approach is introduced using group VIB metals (Cr, Mo, W) supported on sulfated zirconia (SZ) solid acid. It is believed that the Bronsted acidity of SZ should help to convert the dimers generated from metal sites to ethylene and aromatics like benzene.

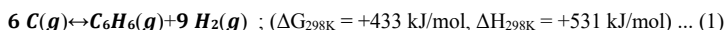
Here, fresh Mo, W and Cr were doped into SZ and characterized using pyridine DRIFTS, ammonia TPD, BET and SEM-EDS.. Catalytic activity for MDHA was ranked as Mo>W>Cr. Mo/SZ showed greater selectivity towards ethylene and benzene, followed by W/SZ, which was selective primarily towards ethylene. Cr/SZ showed the least activity

under similar reaction conditions, producing only a small amount of ethylene. Higher catalytic activity for Mo/SZ was possibly due to reduced Mo oxide sites, found from XANES analysis, as well as higher acidity, observed from TPD. Deactivation was mainly due to coking, observed from subsequent TPO analysis. Further investigation is necessary to enhance the activity of this novel catalytic approach before considering for potential industrial applications.

INTRODUCTION

The growing need of heavier hydrocarbons in chemical industries has reached a new height in the 21st century. Natural gas is a cleaner source of high value chemicals compared to other conventional fossil fuels such as coal & oil. Unfortunately, conventional end use of natural gas includes power generation and flaring[1]. To make the best use of this abundant natural resource, research has been focused on activating natural gas components with minimal energy input. Major component of natural gas is methane, which has been well studied as a feedstock for producing valuable chemicals using heterogeneous catalysts.[2, 3] Methane conversion process can be categorized into direct and indirect reaction routes[2]. The difference is that for the indirect process, an intermediate product formation, typically syngas, is required[4]. This additional reaction step is used to produce higher hydrocarbons but is energy intensive. Direct conversion is advantageous because it eliminates the intermediate step[5], while greatly reducing energy requirements and capital investment. Primary challenge for direct conversion is activating the first C-H bonds of methane, which is thermodynamically very stable[2]. To overcome such high activation barrier, presence of a catalyst is necessary.

One such reaction mechanism involves activating methane using a bifunctional catalyst having two adjacent active sites, known as methane dehydroaromatization (MDHA). Transition metals of group VIB (Mo, W) have shown alkane activation via this route.[6]



Mo oxide supported on ZSM-5/MCM-22 is a well-studied bifunctional catalyst for MDHA.[7, 8] It has been reported that the metal carbide species produced from Mo/W oxides activate methane by forming CH_x species, which is dimerized into C₂H_y species.[9] The acidic sites present on ZSM-5/MCM-22 are believed to be responsible for oligomerization of the C₂H_y species to form benzene and heavier aromatics [5].

Solid heterogeneous catalysts[10] can catalyze a range of reactions. Even though homogeneous acid catalysts are advantageous for higher reaction rates at low temperature reactions [13, 16], for certain reaction systems high temperature solid acids are required. This allows to overcome the thermodynamic limitations associated with low temperatures. [15].

Solid acids such as sulfated zirconia (SZ), sulfated hafnia (SH), tungstated zirconia (WZ) are highly acidic, thermally stable compounds [11]. These possess strong BA sites[12] that have a key role in the oligomerization of dimeric species. Among the sulfated oxide based super acids, sulfated ZrO₂ has been most frequently investigated, modified, and applied to various reaction systems[13-16], because of their strong acid sites, ease of preparation, and commercial availability.

Group VIB metal (Mo, W, Cr) doped on solid acids has been reported for reactions such as alkane direct activation[17, 18], hydroconversion, isomerization [19]

Different amount of loading, calcination technique, catalytic pretreatment, and reaction temperature have been studied the active oxidation state of Mo in a reaction[9]. One of the significant properties of group VIB metals is in the formation of carbides through the addition of carbon into their lattice structure. In excited state the outer d band of these has electron vacancy, which is filled by the valence electron of carbon. This metallic band type appearance lets such metals to have a density of states at the Fermi level which resembles the electronic configuration of a noble metal[20], enabling these to participate in different catalytic reactions as active components.

Keeping these in mind, our goal is to use group VIB based metals, i.e., Mo, W, Cr, and load these onto sulfated zirconia (SZ) solid acid (Figure 1) and compare their performance in MDHA. SZ replaces the conventional acidic ZSM-5/MCM-22 support, which has been well studied for its strong acidic sites that can catalyze cyclization of the C_2H_y dimers generated from the active metal sites[19]. Even though SZ does not possess shape selectivity like HZSM-5, the acidity is believed to be enough to oligomerize the dimers to aromatics[21].

To our knowledge, group VIB metals have never been supported on SZ solid acid and tested for MDHA. The fresh synthesized catalysts are characterized using pyridine DRIFTS, ammonia TPD, SEM-EDS, BET, XANES. The catalysts were then tested for MDHA. Deactivation was studied using temperature programmed oxidation (TPO).



Figure 1: Proposed reaction mechanism for MDHA [M= group VIB metals-W, Mo, Cr]

EXPERIMENTAL

Catalyst synthesis

Conventional literature methods were used to prepare sulfated zirconia. Zirconium oxide was obtained directly from vendors. 1 M H_2SO_4 was added to zirconium

oxide, followed by stirring for 2 hours. This was dried at 110⁰C overnight and calcined at 550⁰C to prepare the final SZ catalyst.

Incipient wetness impregnation method was used to dope 5 wt. % of each metal in SZ. SZ powder and metal precursors were added to make a DI water solution, which was stirred for 2 hours, followed by filtration with excess water. The retentate was dried at 110⁰C overnight and calcined at 550⁰C for 4 hours in ambient condition and stored in bottles to avoid air and moisture exposure.

Catalytic characterization

Physico-chemical properties

The surface area of the catalysts was determined using BET physisorption technique. It was found that in each case, surface area decreased with the addition of metals in SZ surface (Table 1). SZ is reported to have surface area of 50-100 m²/g[13, 22], similar to what was observed in BET analysis. When group VIB metals were added, this surface area decreases, likely due to SZ pore blockage due to metal loading. SEM-EDS analysis was carried out to determine the metal compositions. It was found that the actual amount of metals was lower than that was intended, possibly lost during calcination stage of synthesis.

Table 1: Physico-chemical properties of prepared catalysts

Sample	metal wt.% (intended)	metal wt.% (SEM-EDS)	BET surface area (m ² /g)
SZ	-	-	84
5% W/SZ	5	4.3	71
5% Mo/SZ	5	4.5	76
5% Cr/SZ	5	3.9	74

Pyridine DRIFTS

DRIFTS was carried out using pyridine as weak base probe molecule to determine the acid site stability, before and after the metals were loaded in SZ. Adsorbed pyridine sites on SZ correspond to either Brønsted, Lewis acid sites or dual acid sites. Vibrations at around 1445 cm⁻¹ and 1610 cm⁻¹ represent Lewis acid sites, whereas vibrations at around 1545 cm⁻¹ and 1645 cm⁻¹ represent Brønsted acid sites[23]. Vibrations at around 1495 cm⁻¹ represents sites that contain both Lewis and Brønsted acidity [23, 24]. All these characteristic bands were observed in the four SZ catalysts, indicating that surface acidity remained stable after metals were loaded (Figure 2). All catalysts were tested up to 400⁰C, and stable acid sites were observed as temperature was increased.

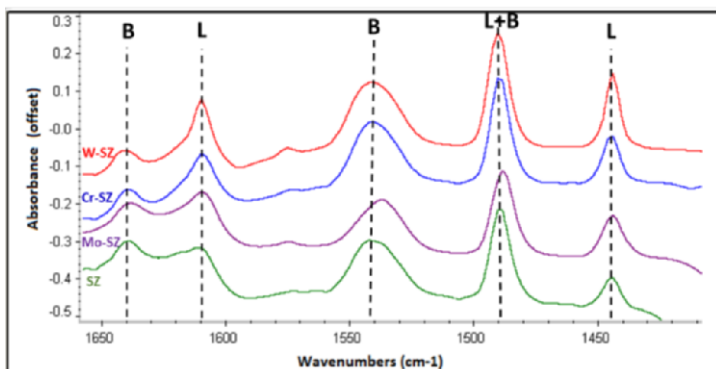


Figure 2: Pyridine DRIFTS of the prepared catalysts: SZ, Mo-SZ, Cr-SZ and W-SZ, each tested at 400°C after pyridine exposure for 3 hours

Ammonia TPD

Ammonia TPD was used to quantify the total acidity of the prepared catalysts. Ammonia was used as probe molecule to study the total acid sites for each catalyst. After analyzing TPD areas, decrease in total acidity was observed for the metal loaded catalysts (Table 2). This suggests that some acid sites were compromised due to metal-support interactions, resulting in a loss of acidity.

Table 2: Amount of NH₃ desorbed/consumed per gram of catalyst

Catalyst	Total micromoles of NH ₃ desorbed per gram catalyst
SZ	1954
5% W/SZ	1133
5% Mo/SZ	1465
5% Cr/SZ	1028

Experimental procedure

The bifunctional catalysts were run at 700°C for ~15 hours to investigate methane dehydroaromatization. The catalysts were first reduced under H₂ flow till the desired reaction temperature was reached. The catalysts were further reduced by introducing a methane to H₂ gas ratio of 1:4, which was flowed into the reactor for 4 hours to achieve the carburized phase.

RESULTS AND DISCUSSION

All three group VIB catalysts were tested at 700°C for MDHA and their activity and product selectivity were measured. Products observed in all the catalytic runs were primarily ethylene and benzene, with small amount of ethane, propylene, propane (not shown). Considerable differences in initial activation periods were observed for all three catalysts, followed by deactivation. At the conditions tested here, deactivation was inevitable due to coking.

Methane conversion and selectivity towards aromatics differed significantly among the three catalysts. This can be attributed to dispersion and concentrations of metal carbide species, as well as the difference of reactivity among the metal species present in SZ. Methane conversion was the highest for Mo-SZ at 700°C, followed by W and Cr, both showing similar activity (Figure 3). It appears that W and Cr oxide in their reduced states are not as stable as the reduced Mo oxides on SZ support at 700°C, which are considered to be the active sites for production of C₂ dimers in MDHA[1, 2, 25]. This is evident during ethylene formation as well, where Mo/SZ showed higher selectivity towards the production of ethylene (Figure 4), followed by W/SZ. Compared to Mo/SZ and W/SZ, Cr/SZ showed lower ethylene selectivity for MDHA, possibly because Cr oxide was not reduced to its active state. Ethylene selectivity was stable for all three catalysts after ~500 mins into reaction.

Only Mo/SZ showed significant benzene selectivity (Figure 5) for MDHA. A possible reason for less aromatization activity observed in W and Cr/SZ might be due to their low acidity, as observed in ammonia TPD, where W and Cr showed lower amount of acidity. More acidity was observed for Mo/SZ, suggesting more acid sites available for the dimers to oligomerize and thus producing more aromatics. Benzene selectivity for Mo/SZ decreased with time, likely due to coke deposition.

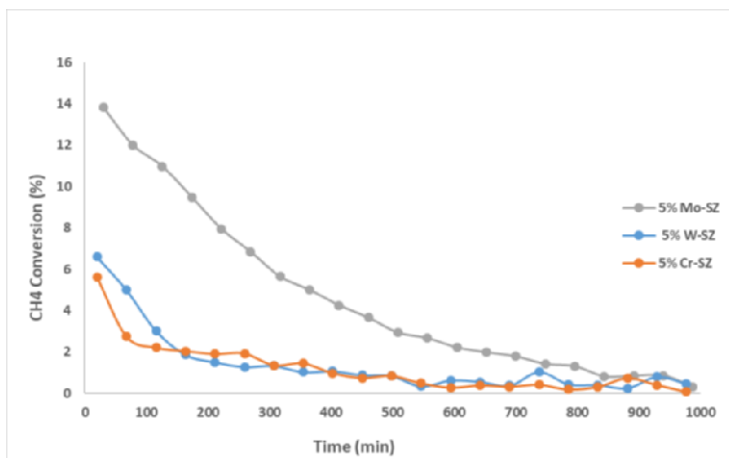


Figure 3: Reaction data of group VIB SZ catalysts for methane conversion (10 sccm CH₄, 700°C, 1 atm, 600 ml/gcat-hr)

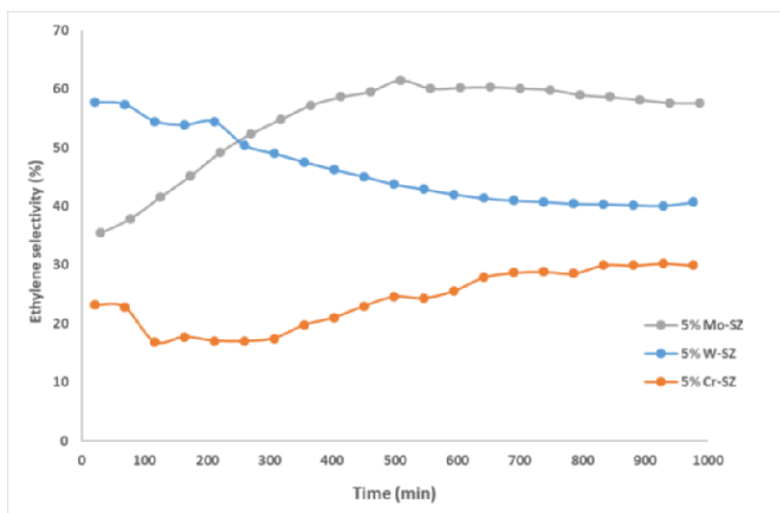


Figure 4: Reaction data of group VIB SZ catalysts for ethylene production (10 sccm CH₄, 700°C, 1 atm, 600 ml/gcat-hr)

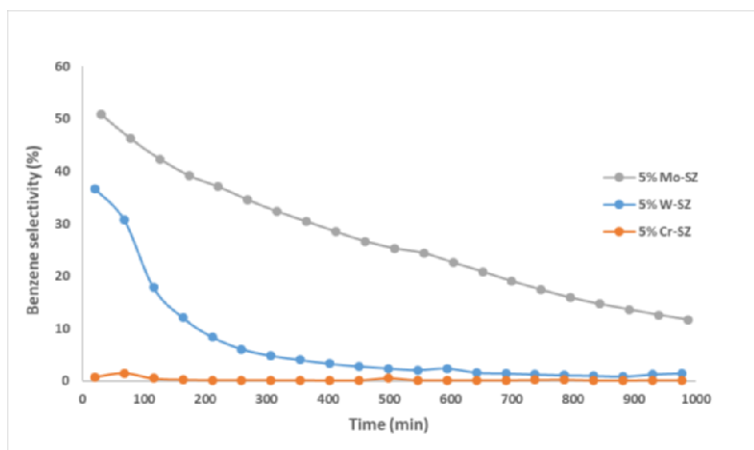


Figure 5: Reaction data of group VIB SZ catalysts for benzene production (10 sccm CH₄, 700°C, 1 atm, 600 ml/gcat-hr)

L_{III} edge XANES: Mo active phase

To understand the reason of such high activity of Mo/SZ compared to the other catalysts, L_{III} edge XANES was carried out on Mo/SZ for investigation of Mo oxidation states during reaction. Fresh, carburized and spent forms of Mo/SZ were compared with

the standard Mo oxide(a) and Mo₂C(e) samples. Fresh Mo/SZ catalyst shows resemblance with the MoO₃ standard, with two split peaks (B and C). These unique splits refer to t_{2g} and e_g splitting of Mo 4d orbitals[26] from tetrahedral coordination. From the XANES analysis, a gradual loss in this characteristic Mo oxide split peak is observed[27], as the catalyst transforms from fresh>carburized>spent phase, indicating reduction of Mo oxide phase towards Mo carbide or oxycarbide[17, 21]. This suggests that Mo oxide was reduced and transformed to Mo carbide/oxycarbide phase, which is regarded as the active site for MDHA[17, 28].

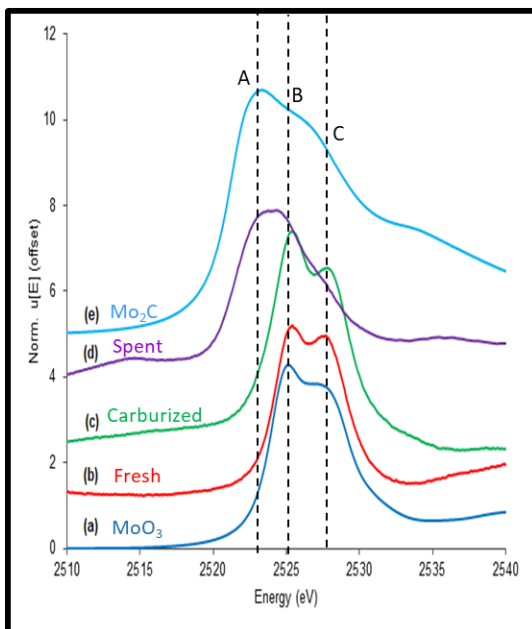


Figure 6: L_{III} edge XANES spectra for catalysts and reference samples (at 50 Torr with eV range of 2510-2540 in transmission mode) : (a) MoO₃ standard, (b) Fresh 5% Mo/SZ (oxidized state), (c) Carburized 5% Mo/SZ, (d) Spent 5% Mo/SZ, (e) Mo₂C standard

Temperature programmed oxidation (TPO)

To investigate catalytic deactivation, TPO was carried out on three metal loaded SZ catalysts. Figure 7 shows the TPO curves for the three catalysts. As observed from the figure, Mo/SZ showed a large peak of carbon at around 500°C. Carbon found at this temperature region (450-550°C) is typically considered to be amorphous in nature[29]. This peak is due to the formation of aromatics. Benzene is a known precursor of coke[30], which makes coke production a sequential reaction pathway from benzene. The more active the catalyst, the more benzene is produced, and ultimately coke is formed. Small carbon peaks were observed for lesser active W/SZ and Cr/SZ spent catalysts at around 550°C, which are also amorphous type.

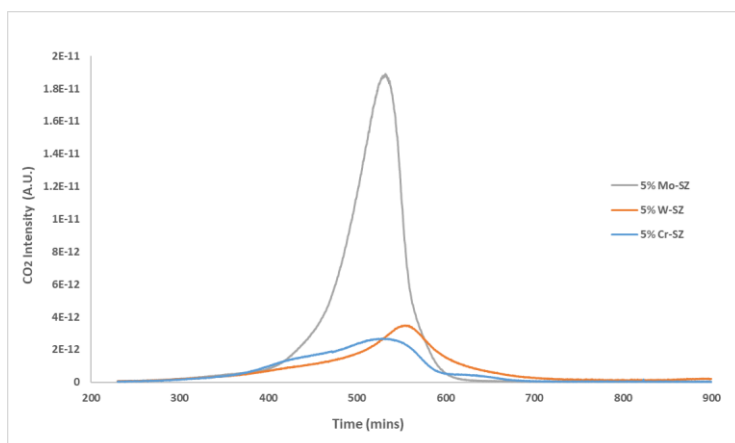


Figure 7: TPO profiles of the spent catalysts, 50 mg, 30 sccm 10% O₂/Ar, 1 atm

CONCLUSION

In this work, group VIB metals (Cr, Mo,W) supported on SZ were characterized and tested for MDHA. The purpose is to evaluate the performance of these catalysts in MDHA activity and product selectivity. BET physisorption showed surface area was lost as metals were loaded onto SZ and caused SZ pore blockage. SEM-EDS showed the actual loading of metals were lower than what was intended, possibly due to a loss during calcination. Pyridine DRIFTS and ammonia TPD showed that SZ acid sites were found to be stable, even though a loss was observed in total acidity after metal loading. Reaction data showed Mo/SZ to be the more active catalyst in terms of activity as well as ethylene and benene selectivity compared to W/SZ and Cr/SZ. This higher Mo/SZ activity is believed to be due to higher acidity[21] as well as reduction in Mo oxide phase, confirmed with XANES. TPO showed higher carbon deposition for Mo/SZ due to higher production of its precursor benzene.. This study shows that Group VIB metals can be used to compare the MDHA reaction as one approach to direct conversion of methane. Possible future work involves more characterization to learn about the deactivation mechanism, e.g., correlation of the fresh and spent catalyst acidity and coke precursors.

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References

- [1] H. Chen, L. Li, J. Hu, Upgrading of stranded gas via non-oxidative conversion processes, *Catal. Today*, (2017) Ahead of Print.
- [2] J.J. Spivey, G. Hutchings, Catalytic aromatization of methane, *Chem Soc Rev*, 43 (2014) 792-803.
- [3] X. Cai, Y.H. Hu, Advances in catalytic conversion of methane and carbon dioxide to highly valuable products, *Energy Science & Engineering*, 7 (2019) 4-29.
- [4] S. Bhattar, M.A. Abedin, D. Shekhawat, D.J. Haynes, J.J. Spivey, The effect of La substitution by Sr- and Ca- in Ni substituted Lanthanum Zirconate pyrochlore catalysts for dry reforming of methane, *Applied Catalysis A: General*, 602 (2020) 117721.
- [5] C. Karakaya, R.J. Kee, Progress in the direct catalytic conversion of methane to fuels and chemicals, *Progress in Energy and Combustion Science*, 55 (2016) 60-97.
- [6] B.M. Weckhuysen, D. Wang, M.P. Rosynek, J.H. Lunsford, Conversion of Methane to Benzene over Transition Metal Ion ZSM-5 Zeolites: I. Catalytic Characterization, *Journal of Catalysis*, 175 (1998) 338-346.
- [7] N. Kosinov, F.J.A.G. Coumans, G. Li, E. Uslamin, B. Mezari, A.S.G. Wijkema, E.A. Pidko, E.J.M. Hensen, Stable Mo/HZSM-5 methane dehydroaromatization catalysts optimized for high-temperature calcination-regeneration, *Journal of Catalysis*, 346 (2017) 125-133.
- [8] M. Rahman, A. Sridhar, S.J. Khatib, Impact of the presence of Mo carbide species prepared ex situ in Mo/HZSM-5 on the catalytic properties in methane aromatization, *Applied Catalysis A: General*, 558 (2018) 67-80.
- [9] T.E. Tshabalala, N.J. Coville, J.A. Anderson, M.S. Scurrell, Dehydroaromatization of methane over Sn-Pt modified Mo/H-ZSM-5 zeolite catalysts: Effect of preparation method, *Applied Catalysis A: General*, 503 (2015) 218-226.
- [10] M.A. Abedin, S. Kanitkar, N. Kumar, Z. Wang, K. Ding, G. Hutchings, J.J. Spivey, Probing the Surface Acidity of Supported Aluminum Bromide Catalysts, *Catalysts*, 10 (2020) 869.
- [11] A. Corma, Solid acid catalysts, *Current Opinion in Solid State and Materials Science*, 2 (1997) 63-75.
- [12] A. Corma, Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions, *Chemical Reviews*, 95 (1995) 559-614.
- [13] B.M. Reddy, M.K. Patil, Organic Syntheses and Transformations Catalyzed by Sulfated Zirconia, *Chemical Reviews*, 109 (2009) 2185-2208.
- [14] A. Rabee, G. Mekhemer, A. Osatiashtiani, M. Isaacs, A. Lee, K. Wilson, M. Zaki, Acidity-Reactivity Relationships in Catalytic Esterification over Ammonium Sulfate-Derived Sulfated Zirconia, *Catalysts*, 7 (2017) 204.
- [15] S. Kanitkar, A. Abedin, S. Bhattar, J. Spivey, Effect of Mo content in methane dehydroaromatization using sulfated zirconia supported Mo₂C catalysts, ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY, AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA, 2018.
- [16] D. Fraenkel, Methane conversion over sulfated zirconia, *Catalysis Letters*, 58 (1999) 123-125.
- [17] M.A. Abedin, S. Kanitkar, S. Bhattar, J.J. Spivey, Mo oxide supported on sulfated hafnia: Novel solid acid catalyst for direct activation of ethane & propane, *Applied Catalysis A: General*, 602 (2020) 117696.
- [18] M.A. Abedin, S. Kanitkar, S. Bhattar, J.J. Spivey, Promotional Effect of Cr in Sulfated Zirconia-Based Mo Catalyst for Methane Dehydroaromatization, *Energy Technology*, 8 (2020) 1900555.
- [19] F.F. Oloye, A.J. McCue, J.A. Anderson, n-Heptane hydroconversion over sulfated-zirconia-supported molybdenum carbide catalysts, *Applied Petrochemical Research*, 6 (2016) 341-352.
- [20] J.B. Claridge, A.P.E. York, A.J. Brungs, C. Marquez-Alvarez, J. Sloan, S.C. Tsang, M.L.H. Green, New Catalysts for the Conversion of Methane

- to Synthesis Gas: Molybdenum and Tungsten Carbide, *Journal of Catalysis*, 180 (1998) 85-100.
- [21] S. Kanitkar, M.A. Abedin, S. Bhattar, J.J. Spivey, Methane dehydroaromatization over molybdenum supported on sulfated zirconia catalysts, *Applied Catalysis A: General*, 575 (2019) 25-37.
- [22] K. Arata, Solid Superacids, in: D.D. Eley, H. Pines, P.B. Weisz (Eds.) *Advances in Catalysis*, Academic Press 1990, pp. 165-211.
- [23] E.P. Parry, *An Infrared Study of Pyridine Adsorbed on Acidic Solids. Characterization of Surface Acidity*, 1963.
- [24] W.-H. Chen, H.-H. Ko, A. Sakthivel, S.-J. Huang, S.-H. Liu, A.-Y. Lo, T.-C. Tsai, S.-B. Liu, A solid-state NMR, FT-IR and TPD study on acid properties of sulfated and metal-promoted zirconia: Influence of promoter and sulfation treatment, *Catalysis Today*, 116 (2006) 111-120.
- [25] P.M. Bijani, M. Sohrabi, S. Sahebdehfar, Thermodynamic Analysis of Nonoxidative Dehydroaromatization of Methane, *Chemical Engineering & Technology*, 35 (2012) 1825-1832.
- [26] S.J. George, O.B. Drury, J. Fu, S. Friedrich, C.J. Doonan, G.N. George, J.M. White, C.G. Young, S.P. Cramer, Molybdenum X-ray absorption edges from 200 to 20,000eV: The benefits of soft X-ray spectroscopy for chemical speciation, *Journal of Inorganic Biochemistry*, 103 (2009) 157-167.
- [27] E.J. Lede, F.G. Requejo, B. Pawelec, J.L.G. Fierro, XANES Mo L-Edges and XPS Study of Mo Loaded in HY Zeolite, *The Journal of Physical Chemistry B*, 106 (2002) 7824-7831.
- [28] M.A. Abedin, S. Kanitkar, S. Bhattar, J.J. Spivey, Methane dehydroaromatization using Mo supported on sulfated zirconia catalyst: Effect of promoters, *Catalysis Today*, (2020).
- [29] C.A. Querini, Coke characterization, in: J.J. Spivey, G.W. Roberts (Eds.) *Catalysis: Volume 17*, The Royal Society of Chemistry 2004, pp. 166-209.
- [30] W. Liu, Y. Xu, Methane Dehydrogenation and Aromatization over Mo/HZSM-5: In Situ FT-IR Characterization of Its Acidity and the Interaction between Mo Species and HZSM-5, *Journal of Catalysis*, 185 (1999) 386-392.