

Impact of Mo and W on CrXO₃ (X = Cr, Mo, W) Catalytic Performance in a Propane Non-oxidative Dehydrogenation Process

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Abstract

The impact of molybdenum (Mo) and tungsten (W) on improving the catalytic characteristics of the chromium-based catalyst, Cr₂O₃, was explored in this study. The use of semi-empirical and density functional theory computational methods was deployed to understand the impact of the substitution of the chromium (Cr) with Mo and W on the catalyst, CrXO₃ (where X = Cr, Mo, W) in the production of propylene from propane. Findings from the investigation confirmed that the surface modified with Mo showed better potential for improving the catalyst selectivity, retarding propylene dehydrogenation, cracking, and coking path than W, which offered a lower selectivity. The use of Mo was found to have better facilitated the propylene production due to its lower affinity for coke and cracking promoting adsorbates accounted for its sites, including easier desorption of propylene and higher barrier of deep dehydrogenation for preventing the production of undesired products, unlike the use of W. This study, therefore, recommends the use of Mo for the improvement of the catalyst that could result in better propylene yield, which could aid in meeting its rising market demand.

Keywords

Molybdenum, tungsten, chromium, catalysis, propane dehydrogenation, catalyst performance, selectivity

1 Introduction

Propylene has been reported to be one of the essential feedstocks or precursors in the production of different petrochemicals. These petrochemicals include polypropylene, isopropanol, propylene oxide, polyol, glycol ethers, acrylonitrile, acrylic acid, epoxy resins, alkyl chlorides, and many other valuable materials.^{1–3} Moreover, a recent survey of the propylene market demand indicated a significant rise over the years due to the diverse petrochemical industries that require propylene for the production of a wide range of materials.^{1,4–7}

The quest to address this rising trend of the propylene market demand^{5–7} has attracted the attention of researchers to give preferential focus on the search for a solution. Some works have considered exploring diverse ways of improving the yield of existing technologies and redesigning the existing catalysts to enhance their activity, selectivity, and rate of catalyst deactivation. The survey of reports in the literature reveals that many researchers across the globe have been giving this subject significant attention. However, the literature shows that studies were primarily concentrating their investigations on using platinum-based catalysts.^{8–18} Only a few studies gave preferential attention to chromium-based catalysts,^{19–32} while some have investigated other catalyst forms like zeolite, nickel, gallium oxide, and many others.^{33–36} Existing reports show that some works deployed an experimental approach to study the catalysts. In contrast, others employed advanced computational methods like

process modelling, molecular modelling, kinetics modelling, and many others.

A survey of the computational studies in the literature also indicates that the bulk of the reports focuses more on the study of platinum-based catalysts than chromium-based catalysts, which claim a lower contribution. Among the few studies that have reported on the use of chromium-based catalysts is the report of Oyegoke et al.,²⁸ which indicated that the chromium site played a significant role in controlling the reaction compared to the oxygen site on the Cr₂O₃ catalyst. Another report²⁹ showed that highly concentrated chromium sites on the chromium-based catalyst can promote deeper dehydrogenation, cracking the intermediates to undesired products. It was further reported that the reaction paths with moderate chromium site participation favoured better selectivity for propylene production.³¹ The report of Hus et al.³⁷ further indicated that high temperature, high pressure, and prolonged propylene accumulation on the catalyst promotes its deactivation. These reports suggest the need to investigate the impact of substituting the chromium site with other metals. Liu et al.²⁷ attempted to use Zn on Cr₂O₃ in the dehydrogenation of propane into propylene, where it was seen to have improved its selectivity.

This study, therefore, attempted to deploy a combined use of Density Functional Theory (DFT) and Parametric Method 3 (PM3) semi-empirical computational approach to investigate the potential impact of substituting the chromium (Cr) site on a chromium-based catalyst with the use of molybdenum (Mo) and tungsten (W) on the catalytic performance of CrXO₃ (where X = Cr, Mo, W) in a pro-

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pane dehydrogenation process to produce propylene. The findings would go a long way to provide insight into the impact of having a moderate concentration of chromium sites on the catalyst, and methods of advancing the catalyst performance to obtain a better propylene yield that could meet the rising market demand for propylene.

2 Materials and methods

2.1 Computational methodology details

The structures were built and minimised using the molecular mechanics (MMFF) method to remove strain energy,^{38,89} after which the resulting structure was used as initial geometry during the use of DFT where B3LYP calculation method with 6-31G* and LANL2DZ basis sets were adopted, in line with the existing reports.^{29,31} In using semi-empirical theory, the PM3 method was also used to optimise another set of the built structures where respective minimised structures were used as the structure for initiating the PM3 semi-empirical calculation. Existing literature^{40,41} has justified using the PM3 and B3LYP method for the chromium and transition metals-based systems. The equilibrium optimised geometry used ensured that the structures built showed no negative imaginary frequency on the infrared (IR) spectra results. As for the transition-state geometry search, it was ensured that the structures built do show only one negative imaginary frequency on the infrared (IR) spectra results. The computations were carried out using Spartan 18' molecular simulation application on Dell Precision 3520 with 8 GB RAM, Intel Core i7 processor with 2.8 GHz and 512 GB storage.

2.2 Impact of tungsten and molybdenum on the performance of the catalyst in the dehydrogenation processes

This analysis evaluated different surface affinities for the coking, cracking, and other dehydrogenation paths' adsorbates like methylidene, propyl, propylene, and propylidene, as well as the catalyst selectivity for the propylene desorption from the catalyst instead of further dehydrogenation of propylene using computational methods stated in the earlier section.

2.2.1 Adsorption energy computation for the selected adsorbate across the surfaces

The analysis entailed the evaluation of the propyl, methylidene, propylene, and propylidene adsorption strength, where the result for the strength of the propyl and methylidene was used to draw insight into the potential of the surface to promote cracking and/or coking process when a relative stronger affinity is identified for the surface when compared to the unmodified surface. Propylidene adsorption strengths were used to ascertain the maximum level of barrier that the surface can offer for inhibiting the path leading to deep dehydrogenation. In contrast, propylene adsorption energies were used to determine the energy demand required in desorbing the propylene off

the surface. The respective adsorption strengths were evaluated using the expression, Eq. (1),

$$E_{\text{ads}} = E_{\text{mx}} - E_{\text{m}} - E_{\text{x}}, \quad (1)$$

where E_{ads} is the adsorption strength, E_{mx} is the total energy of the catalyst with adsorbate, E_{m} is the total energy of the adsorbate, and E_{x} is the total energy of the catalyst.

2.2.2 Analysis of catalyst selectivity

The impact of introducing molybdenum (Mo) and tungsten (W) on the chromium oxide catalyst selectivity was evaluated as the ratio of deep dehydrogenation (propylene dehydrogenation) activation energies, $E_{\text{a,PDAr}}$, and propylene desorption energies, E_{des} (which was computed as the negative of adsorption energies or strengths), where ratios ($E_{\text{a,PDAr}}/E_{\text{des}}$) lesser than 1 indicate poor selectivity. In contrast, a catalyst with ratios greater than one was confirmed as good selectivity. This evaluation approach denoted that the higher the ratio, the better the catalyst selectivity. The activation energies, $E_{\text{a,PDAr}}$, were computed via the difference in transition-state and intermediate energies.

3 Results and discussion

The results collected for the study of the impact of molybdenum and tungsten on the performance of the chromium-based catalyst are presented in two sections. Section 3.1 presents the findings from the evaluation of the adsorption strength for the coking and cracking adsorbate. Section 3.2 reports on the selectivity of the catalyst for the desorption of propylene during the propane dehydrogenation over the path of deep dehydrogenation leading to propylidene.

3.1 Evaluation of different chromium-based catalysts' binding strength for coking and cracking adsorbate species as a path to catalyst deactivation

The results obtained for assessing chromium-based catalysts' binding strength for different species (propyl, methylidene, propylene, and propylidene) lead to cracking and coking in the dehydrogenation of propane into propylene, as shown in Fig. 1(a-d). The more negative the adsorption energy value, the higher the adsorption strength of the surface/catalyst for the concerned adsorbates like propyl, methylidene, propylene, and propylidene. The relationship between results obtained from PM3 and DFT method for the adsorption strengths is presented in Fig. 1(a-d).

The study of the results (in Fig. 1a) collected for the adsorption of propyl across different catalysts presented the strength in the order: CrWO₃ (highest) > Cr₂O₃ > CrMoO₃ (lowest). The binding strength of the catalyst surfaces for propylene was found to have also followed a similar trend reported for propyl adsorption. Moreover, it was also deduced that the introduction of Mo decreased the propyl and propylene adsorption strength. In contrast, the intro-

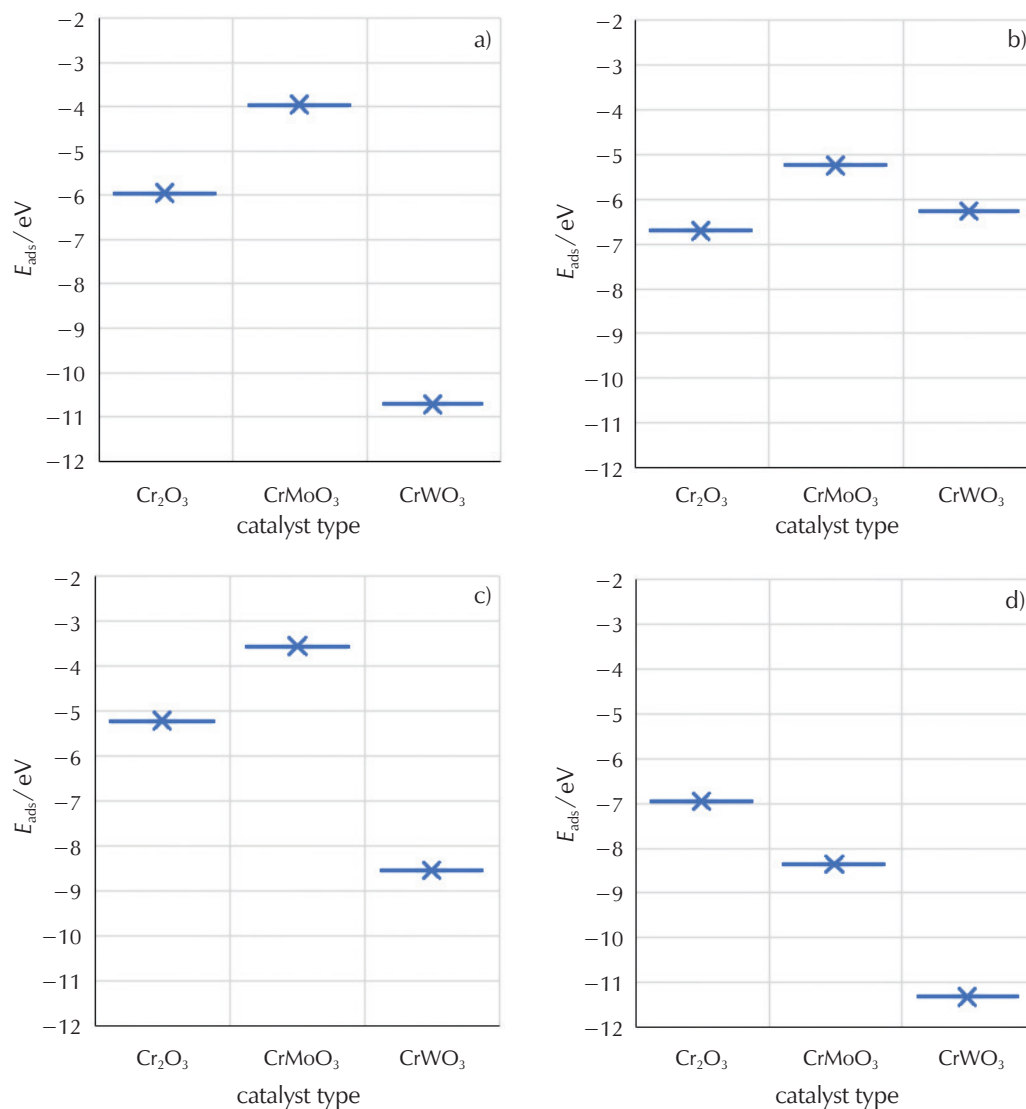


Fig. 1 – Adsorption strength (E_{ads}) for the different coking and cracking adsorbates across different chromium-based catalysts from the DFT method: (a) propyl, (b) methylidene, (c) propylene, and (d) propylidene

duction of W increased the propyl and propylene adsorption strength on chromium-based catalysts, since W-based catalysts displayed more negative values, implying a higher adsorption strength for the adsorbate. The introduction of W on the surface made propylene desorption difficult, which has the potential of promoting cracking of the propyl species due to its stronger bind force for such adsorbate on its surface, unlike the introduction of Mo, which was found to be less demanding due to the lower adsorption strength reported for the modified chromium-based catalyst matrix. Similar deductions were also obtained for using the PM3 calculation method (Fig. 2), showing that Mo's use was preferable due to the lower adsorption energy reported for its surface, which agreed with *S. M. Al-Zahrani*⁴³ report demonstrating Mo catalytic behaviour in propylene production.

Furthermore, a study of the results presented in Fig. 1b for the methylidene adsorption across different surfaces was found to have followed the trend: Cr₂O₃ (highest) > CrWO₃ > CrMoO₃ (lowest). The introduction of Mo was found to have reduced the surface affinity for the methylidene, which is well known as a coking adsorbate assessed to identify potential surfaces retarding coking rate by showing a character with a lower affinity for coking species. Similarly, the findings obtained from the DFT calculation agreed with the PM3 calculation (Fig. 2) despite the difference in the trend confirming the use of Mo to be much better due to its lower affinity for the methylidene on its surface, unlike the surface modified with the use of W. The results were in accordance with the experiment^{43,44} reporting that the use of Mo is promising. This suggests that substituting some Cr site on the catalyst with Mo has been predicted to prevent methylidene adsorption, leading to deactivation.

The adsorption of propylidene across the catalyst surface was found to have also followed the trend: CrWO₃ (highest) > CrMoO₃ > Cr₂O₃ (lowest). Findings from the analysis (in Fig. 1d) indicated that the introduction of W strengthened the deep dehydrogenation of propylene into propylidene, unlike the other surface with Mo or surfaces without new (or foreign) metals, due to the lower negative values reported for the adsorption energy, implying that chromium oxide catalyst modified with W would bind propylene stronger to the surface making it challenging to desorb propylene from the catalyst surface. The deductions from the DFT calculation agreed with the PM3 calculation despite the difference in the trend, showing W to be the worst, retarding the propylene desorption from catalyst surface, unlike the one with Mo.

The difference in the trend reported for the use of PM3 and DFT can be associated with the different levels of accuracy that each method could offer in various analyses

(Fig. 3). However, a good relationship was reported for the computation of the adsorbate evaluated, except for the methylidene, which showed a different trend and relation. A linear relationship was obtained for the PM3 and DFT computation of propyl, propylene, and propylidene adsorption energies, displaying R^2 values of 0.9828, 0.9967, and 0.9310. In contrast, methylidene adsorption was non-linear, showing a quadratic relationship with an R^2 value of 1.000, and poor linear relation (with an R^2 value of 0.0628). The poor linearity identified for the used PM3 with that of the DFT could be attributed to the higher accuracy reported for the use of DFT over that of the semi-empirical approach in the literature⁴⁵ that indicated that the prediction of DFT is closer to more experiment compared to PM3.

In general, the findings from this study confirm that Mo binding force for propylene was found to be lower, showing much lower desorption energy, unlike other forms of

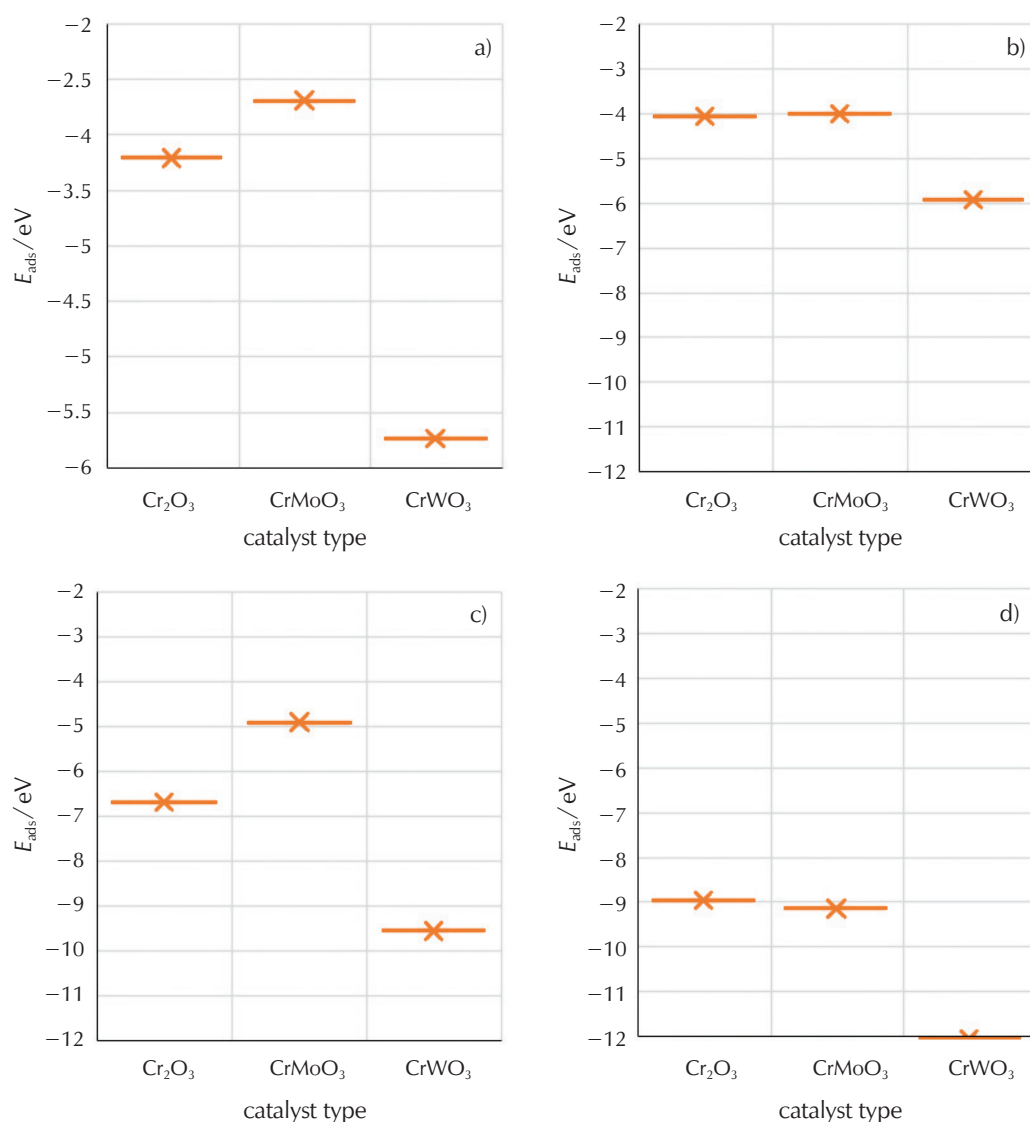


Fig. 2 – Adsorption strength (E_{ads}) for the different coking and cracking adsorbates across different chromium-based catalysts from the PM3 Method: (a) propyl, (b) methylidene, (c) propylene, and (d) propylidene

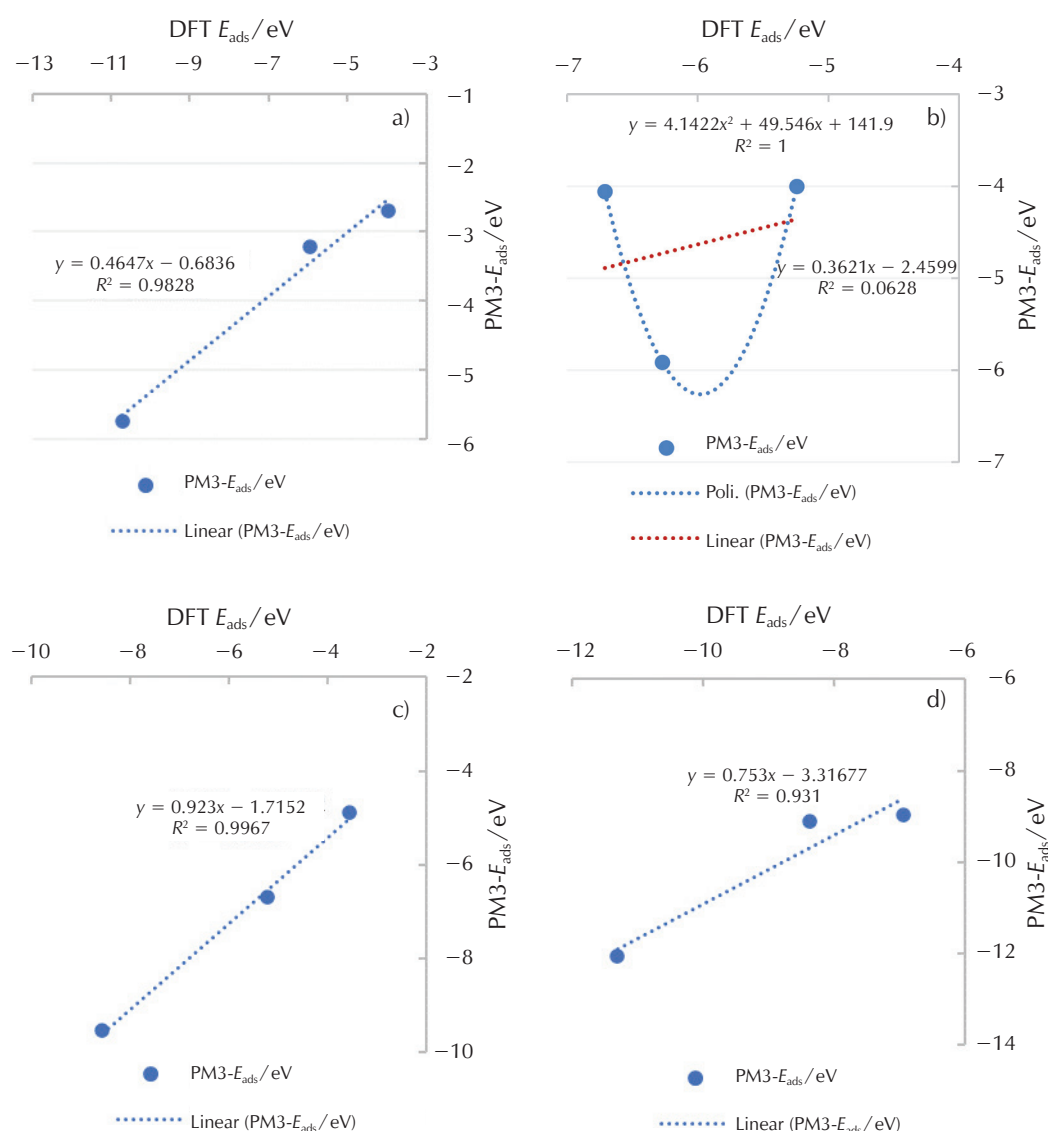


Fig. 3 – Relationship between adsorption strengths obtained via DFT and PM3 calculation obtained for the different coking and cracking adsorbates across different chromium-based catalysts: (a) propyl, (b) methylidene, (c) propylene, and (d) propylidene

catalyst matrices where W was used showing higher desorption energy. Likewise, adsorption strength for the deep dehydrogenation product (propylidene) and coking product (methylidene) indicated that Mo displayed the most negligible value from PM3 and DFT computations. Therefore, deductions from the study confirm the use of Mo to have best improved the performance of the chromium oxide catalyst, other than the use of W, based on the adsorption study carried out for the key species involved in the cracking dehydrogenation of propane.

3.3 Catalyst selectivity between product desorption and deep dehydrogenation in the presence of molybdenum (Mo) and tungsten (W)

The results obtained for the analysis of catalyst selectivity, S ($E_{a,PDA}/E_{des}$) are presented in Table 1, where E_{des} denotes the propylene desorption energy, $E_{a,PDA}$ denotes the propylene

Table 1 – Comparison of propane desorption with deep dehydrogenation using the DFT method

Catalyst	$E_{a,PDA}/\text{eV}$	E_{des}/eV	MCr Sites	S ($E_{a,PDA}/E_{des}$)
Cr ₂ O ₃	4.68	5.22	CrCr	0.90
CrMoO ₃	5.59	3.56	MoCr	1.57
CrWO ₃	4.02	8.55	WCr	0.47

(or deep) dehydrogenation activation energy, and MCr denotes the metallic sites that provided the higher barrier for hindering the possibility of further dehydrogenating propylene into propylidene.

The selectivity of the catalyst was found to have improved with the introduction of molybdenum (Mo) in the chro-

mium oxide catalyst with a ratio of $S = 1.57$ other than the use of tungsten (W), where the selectivity for the desorption of propylene from the catalyst was found to be poor displaying a much lower ratio of $S = 0.47$. Findings from this study imply that the use of Mo improved the catalyst's selectivity for propylene desorption compared to the use of W, which displayed a better selectivity for deep dehydrogenation of propylene. The deductions were in agreement with the literature reports^{42,43} which indicated that the introduction of molybdenum as a promoter to different catalysts had primarily improved the catalytic performance. One of the reports⁴³ showed that propane dehydrogenated in the presence of a Cr-based catalyst at 623 K yielded 31.7 % propylene. Still, with the introduction of molybdenum, its propylene yield was improved to 76.8 % using a Cr : Mo ratio of 2 : 4. *Otroshchenko et al.*⁴² report further confirmed improving a vanadium-based catalyst via the introduction of molybdenum, resulting in 36 % propane conversion and 89 % propylene selectivity, which was relatively high compared to the other forms of vanadium-based catalyst without Mo. The two reports^{42,43} showed good relation with the current study's findings, which confirmed that CrMoO₃ had demonstrated a higher potential for propylene production and lower potential to facilitate the cracking reaction. The deduction for introducing Mo to chromium oxide (CrXO₃) catalyst to give CrMoO₃ implies that this would contribute to retarding the rate of catalyst deactivation and thereby improve the catalyst selectivity.

4 Conclusions

A density functional theory and semi-empirical computational methods were successfully deployed in investigating the impact of substituting the chromium (Cr) site on a chromium-based catalyst, CrXO₃ (where X = Cr, Mo, W), with molybdenum (Mo) and tungsten (W) on its resulting catalytic performance in a propane dehydrogenation process to produce propylene.

Findings from the analysis confirmed that the surface modified with Mo displayed better potential for improving the catalyst selectivity and retarding the rate of propylene dehydrogenation, cracking, and coking, unlike W, which showed lower selectivity leading to the production of undesired products. Therefore, the choice of introducing Mo on the catalyst matrix to reduce the domination of the Cr-site would go a long way to accelerate propylene production, due to its lower affinity for coke and cracking promoting adsorbates, including a lower propylene desorption energy and higher deep dehydrogenation barrier for preventing further breaking of the propylene into undesired products like methane, coke, methylidene, propylidene, and many others.

Conflict of Interest

The authors declare no conflict of interest.

List of abbreviations

F	– forward reaction
R	– reverse reaction
des	– desorption step
E_a	– activation energy or energy barrier
E	– electronic energy
Cr	– chromium site
DFT	– density functional theory
E_{ads}	– adsorption energy or strength
IR	– infrared spectra
MMFF	– molecular mechanics force field
Mo	– molybdenum atom
PM3	– parameterized method three approximation of semi-empirical theory
R	– correlation coefficient
W	– tungsten atom
E_{des}	– propylene desorption energy
$E_{a,PDA}$	– propylene (or deep) dehydrogenation activation energy
MCr	– metallic sites that provided a higher barrier for hindering the possibility of further dehydrogenating propylene into propylidene
S	– catalyst selectivity, $S = E_{a,PDA}/E_{des}$
Cr ₂ O ₃	– unmodified catalyst model
CrMoO ₃	– Mo-modified catalyst model
CrO ₃ W	– W-modified catalyst model
E_{ads}	– adsorption strength,
E_{mx}	– energy of the catalyst with adsorbate
E_m	– energy of the adsorbate
E_x	– energy of the catalyst
LANL2DZ	– Los Alamos National Laboratory 2 Double-Zeta
B3LYP	– Becke, 3-parameter, Lee-Yang-Parr

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SAŽETAK

Utjecaj Mo i W na katalitička svojstva CrXO₃ (X = Cr, Mo, W) u procesu neoksidativne dehidrogenacije propana

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S ciljem poboljšanja karakteristika katalizatora na bazi kroma, u ovom su se istraživanju kombinirano primijenile poluempirijske računalne metode i metode temeljene na teoriji funkcionala gustoće. Nastojao se dobiti uvid u katalitički potencijal izmjene kroma molibdenom i volframom u katalizatoru CrXO₃ (gdje X označava krom, molibden i volfram) za dehidrogeniranje propana pri proizvodnji propilena. Rezultati su potvrdili da površina modificirana molibdenom pokazuje bolju selektivnosti u usporedbi s površinom modificiranom volframom, usporavajući dehidrogenaciju, pucanje i koksiranje propilena. Utvrđeno je da upotreba molibdena olakšava proizvodnju propilena zbog njegova nižeg afiniteta prema adsorbatima koji potiču pucanje i koksiranje, uključujući i lakšu desorpciju propilena te višu barijeru potpune dehidrogenacije što sprječava nastanak neželjenih produkata; to nije bio slučaj kod volframa. Ovo istraživanje stoga preporučuje upotrebu molibdena za poboljšanje svojstva katalizatora, što bi moglo rezultirati većim iskorištenjem u proizvodnji propilena te pomoći zadovoljavanju rastuće tržišne potražnje za propilenom.

Ključne riječi

Molibden, volfram, krom, kataliza, dehidrogenacija propana, svojstva katalizatora, selektivnost

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