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

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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. 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.

The quest to address this rising trend of the propylene market demand 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 efforts on using platinum-based catalysts. Only a few studies have given preferential attention to chromium-based catalysts, while some have investigated other catalyst forms like zeolite, nickel, gallium oxide, and many others. 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. which indicated that the chromium site played a significant role in controlling the reaction compared to the oxygen site on the Cr₃O₇ catalyst. Another report 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. The report of Hus et al. 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. attempted to use Zn on Cr₃O₇ 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-
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, 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. 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 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 cracking, coking, 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),

\[ E_{\text{ads}} = E_{\text{mx}} - E_{\text{m}} - E_{\nu} \]  

where \( E_{\text{ads}} \) is the adsorption strength, \( E_{\text{mx}} \) is the total energy of the catalyst with adsorbate, \( E_{\text{m}} \) is the total energy of the adsorbate, and \( E_{\nu} \) 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, \( E_{\text{a,PDA}} \), and propylene desorption energies, \( E_{\text{des}} \) (which was computed as the negative of adsorption energies or strengths), where ratios (\( E_{\text{a,PDA}}/E_{\text{ads}} \)) 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, \( E_{\text{a,PDA}} \), 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: CrWO\(_3\) (highest) > Cr\(_2\)O\(_3\) > Cr-MoO\(_3\) (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-
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’s 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: $\text{Cr}_2\text{O}_3$ (highest) $>$ CrWO$_3$ $>$ CrMoO$_3$ (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 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.

Fig. 1 – Adsorption strength ($E_{\text{ads}}$) 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.
The adsorption of propylidene across the catalyst surface was found to have also followed the trend: CrWO$_3$ (highest) > CrMoO$_3$ > Cr$_2$O$_3$ (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 literature$^{45}$ 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
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, $S \left( \frac{E_{a,PDA}}{E_{des}} \right)$ are presented in Table 1, where $E_{des}$ denotes the propylene desorption energy, $E_{a,PDA}$ denotes the propylene (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-
mum 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\textsuperscript{42,43} which indicated that the introduction of molybdenum as a promoter to different catalysts had primarily improved the catalytic performance. One of the reports\textsuperscript{41} 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. Otroschchenko et al.\textsuperscript{42} report further confirming improved 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\textsuperscript{42,43} showed good relation with the current study’s findings, which confirmed that CrMoO$_3$ had demonstrated a higher potential for propylene production and lower potential to facilitate the cracking reaction. The deduction for introducing Mo to chromium oxide (CrXO$_3$) catalyst to give CrMoO$_3$ 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, CrXO$_3$ (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, methyldiene, propyldiene, and many others.

Conflict of Interest

The authors declare no conflict of interest.
6. J. Mack, Propylene Market Analysis Report 2030: Industry Size, Share, Growth, Key Players, Opportunities, Noida, (Sep. 2021). URL: https://www.datatrendsmarketresearch.com/reports/global-propylene-market (Jan. 29, 2022).

7. DBMR, Propylene Market Size, Share, Growth, Analysis, Price, & Industrial Trends, Data Bridge Market Research Report, 2022. URL: https://www.datadigemarketresearch.com/reports/global-propylene-market (Jan. 29, 2022).

8. A. W. Hauser, P. R. Horn, M. Head-Gordon, A. T. Bell, A systematic study on Pt-based, subnanometer-sized alloy catalysts for alkane dehydrogenation: Effects of intermetallic interaction, Phys. Chem. Chem. Phys. 18 (16) (2016) 10906–10917, doi: https://doi.org/10.1039/C6CP03660E.

9. W. Zhang, H. Wang, J. Jiang, Z. Sui, Y. Zhu, D. Chen, X. Zhou, Size Dependence of Pt Catalysts for Propane Dehydrogenation: From Atomically Dispersed to Nanoparticles, ACS Cat. 10 (21) (2020) 12932–12942, doi: https://doi.org/10.1021/acscatal.0c03286.

10. M. L. Yang, Y. A. Zhu, X. G. Zhou, Z. J. Sui, D. Chen, First-principles calculations of propane dehydrogenation over PtSn catalysts, ACS Cat. 2 (6) (2012) 1247–1258, doi: https://doi.org/10.1021/cs300031d.

11. M. L. Yang, Y. A. Zhu, C. Fan, Z. J. Sui, D. Chen, X. G. Zhou, DFT study of propane dehydrogenation on Pt catalyst: Effects of step sites, Phys. Chem. Chem. Phys. 13 (8) (2011) 3257–3267, doi: https://doi.org/10.1039/c0cp00314g.

12. L. Nykänen, K. Honkala, Selectivity in propane dehydrogenation on Pt and PtSn surfaces from first principles, ACS Cat. 3 (12) (2013) 3026–3030, doi: https://doi.org/10.1021/cs400566y.

13. S. Saerens, M. K. Sabbe, V. v. Galvita, A. E. Redekop, M. F. Reyniers, G. B. Marin, The Positive Role of Hydrogen on the Dehydrogenation of Propane on Pt(111), ACS Cat. 7 (11) (2017) 7495–7508, doi: https://doi.org/10.1021/acs.catal.7b01584.

14. H. Timothy, Comparative study of the catalytic dehydrogenation of propane on Pt and Pt3Ga catalysts, Gent, (2014). URL: https://libstore.ugent.be/fulltext/RUG/001/224/444/RUG01-00224444_2015_0001_AC.pdf (Feb. 20, 2020).

15. M. Santhosh Kumar, D. Chen, J. C. Walmesley, A. Holmen, Dehydrogenation of propane over Pt-SBA-15: Effect of Pt particle size, Cat. Comm. 9 (5) (2008) 747–750, doi: https://doi.org/10.1016/j.catcomm.2007.08.015.

16. Q. Chang, K. Wang, P. Hu, Z. Sui, X. Zhou, D. Chen, W. Yuan, Y. Zhu, Dual-function catalysts in propane dehydrogenation over Pt-GaOx catalyst: Insights from a microkinetic analysis, AIChE Journal 66 (7) (2020) e16232, doi: https://doi.org/10.1002/aic.16232.

17. W. Wannapakdee, T. Yuthalekha, P. Dugkhuntod, K. Rodponenthukwaji, A. Thavisith, S. Nokbin, T. Witoon, S. Pengchan, C. Wattanakit, Dehydrogenation of propane to propylene using promoter-free hierarchical Pt/silicalite-1 nanosheets, Catalysts 9 (2) (2019) 174, doi: https://doi.org/10.3390/ catal9020174.

18. M. Aly, E. L. Fornerio, A. R. Leon-Garzon, V. v. Galvita, M. Saey, Effect of Boron Promotion on Coke Formation during Propane Dehydrogenation over Pt/γ-Al2O3 Catalysts, ACS Catal. 10 (2020) 5208–5216, doi: https://doi.org/10.1021/acs.catal.9b05546.

19. J. Baek, H. J. Yun, D. Yun, Y. Choi, J. Yi, Preparation of highly dispersed chromium oxide catalysts supported on mesoporous silica for the oxidative dehydrogenation of propane using CO2: Insight into the nature of catalytically active chromium sites, ACS Cat. 2 (2012) 1893–1903, doi: https://doi.org/10.1021/cs300198u.

20. S. Lillehaug, K. J. Barve, M. Sierka, J. Sauer, Catalytic dehydrogenation of ethane over mononuclear Cr(II) surface sites on silica. Part I. C-H activation by σ-bond metathesis, in: P. Kolsaker, M.-F. Ruasse (Eds.), J. Phys. Org. Chem. 17, Special Issue: ESOR IX – 9th European Symposium on Organic Reactivity, 12 – 17 July 2003, Oslo, Norway; 2014, pp. 990–1006, doi: https://doi.org/10.1002/poc.842.

21. P. Michorczyk, J. Ogonowski, P. Kuśrowski, L. Chmielarz, Chromium oxide supported on MCM-41 as a highly active and selective catalyst for dehydrogenation of propane with CO2, Appl. Cat. A: Gen. 349 (1–2) (2018) 62–69, doi: https://doi.org/10.1016/j.apcata.2008.07.008.

22. S. Sim, S. Gong, J. Bae, Y. K. Park, J. Kim, W. C. Choi, U. G. Hong, D. S. Park, I. K. Song, H. Seo, N. Y. Kang, S. Park, Chromium oxide supported on Zr modified alumina for stable and selective propane dehydrogenation in oxygen-free moving bed process, Mol. Cat. 436 (2017) 164–173, doi: https://doi.org/10.1016/j.mcat.2017.04.022.

23. T. A. Nijhuis, S. J. Tinnemans, T. Visser, B. M. Weckhuysen, Towards real-time spectroscopic process control for the dehydrogenation of propane over supported chromium oxide catalysts, Chem. Eng. Sci. 59 (2004) 5487–5492, doi: https://doi.org/10.1016/j.ces.2004.07.103.

24. J. Janas, J. Gurgul, R. P. Socha, J. Kowalska, K. Nowinska, T. Shishido, M. Che, S. Dzveigij, Influence of the content and environment of chromium in CrSiBEA Zeolites on the oxidative dehydrogenation of propane, J. Phys. Chem. C 113 (2009) 13273–13281, doi: https://doi.org/10.1021/jp809733s.

25. A. Węgrzyniak, S. Jarzczewski, A. Węgrzynowicz, B. Michorczyk, P. Kuśrowski, P. Michorczyk, Catalytic behavior of chromium oxide supported on nanocasting-prepared mesoporous alumina in dehydrogenation of propane, Nanomat. 7 (2017) 249, doi: https://doi.org/10.3390/nano7090249.

26. J. Gascón, C. Téllez, J. Herguido, M. Menéndez, Propane dehydrogenation over a Cr2O3/Al2O3 catalyst: Transient kinetic modelling of propane and coke formation, Appl. Cat. A: Gen. 248 (1–2) (2003) 105–116, doi: https://doi.org/10.1016/S0926-80X0(03)00128-5.

27. J. Liu, Y. Liu, Y. Ni, H. Liu, W. Zhu, Z. Liu, Enhanced propane dehydrogenation to propylene over zinc-promoted chromium catalysts, Cat. Sci. Tech. 10 (2020) 1739–1746, doi: https://doi.org/10.1039/c9cy01921a.

28. T. Oyegoke, F. N. Dabai, A. Uzairu, B. Y. Jibril, Insight from the study of acidity and reactivity of Cr2O3 catalyst in propane dehydrogenation: a computational approach, B. J. Pur. App. Sci. 11 (1) (2019) 178–181, doi: https://doi.org/10.4314/bjop.v1i11.29s.

29. T. Oyegoke, N. Dabai, A. Uzairu, B. Y. Jibril, Density functional theory calculation of propane cracking mechanism over chromium (III) oxide by cluster approach, J. Serb. Chem. Soc. 86 (30) (2021) 44–44, 2021, doi: https://doi.org/10.2298/jcs200521044a.

30. T. Oyegoke, F. N. Dabai, A. Uzairu, B. Y. Jibril, The Quantum Mechanics Calculation of Molybdenum and Tungsten Influence on the CrM oxide Catalyst Acidicity, HJSE 7 (4) (2020) 297–311, doi: https://doi.org/10.17350/hjse1903000199.

31. T. Oyegoke, F. N. Dabai, A. Uzairu, B. Y. Jibril, Mechanistic insight into propane dehydrogenation into propylene over chromium (III) oxide by cluster approach and Density Functional Theory calculations, Eur. J. Chem. 11 (4) (2020) 342–350, doi: https://doi.org/10.5155/eurjchem.11.4.342-350.2045.
Theo Guo, Propane oxydehydrogenation to propylene over chromium oxide-based catalysts, Appl. Cat. A: Gen. 264 (2) (2004) 193–202, doi: https://doi.org/10.1016/j.apcata.2003.12.054.

C. F. Li, X. Guo, Q. H. Shang, X. Yan, C. Ren, W. Z. Lang, Y. J. Guo, Defective TiO2 for Propane Dehydrogenation, Ind. Eng. Chem. Res. 59 (10) (2020) 4377–4387, doi: https://doi.org/10.1021/acs.iecr.9b06759.

T. K. Katranas, A. G. Vlessidis, V. A. Tsaitouras, K. S. Triantafylidis, N. P. Evmaridis, Dehydrogenation of propane over natural clinoptilolite zeolites, Micr. Mes. Mat. 61 (1–3) (2003) 189–198, doi: https://doi.org/10.1016/S1387-1811(03)00367-6.

T. Saelee, S. Namuangruk, A. Junkaew, Theoretical Insight into Catalytic Propane Dehydrogenation on Ni(111), J. Phys. Chem. C 122 (2018) 14678–14690, doi: https://doi.org/10.1021/acs.jpcc.8b03939.

J. Schäferhans, S. Gõmez-Quero, D. v. Andreeva, G. Roth, PM3 Computational Studies of the Reaction Mechanism for Propane Dehydrogenation, Ind. Eng. Chem. Res. 12256, doi: https://doi.org/10.1021/acs.iecr.8b03939.

Bio-Rad, Chromium(III) oxide – FTIR – Spectrum – SpectraBase, Bio-Rad, SpectraBase BIO-RAD, John Wiley & Sons Inc., Wiley SpectraBase (2021), URL: https://spectrabase.com/spectrum/K4PRBHxDI (Mar. 09, 2021).

J. H. Warren, A Guide to Molecular Mechanics and Quantum Chemical Calculations. Wavefunction, Irvine, CA, USA, 2003, URL: http://mms.dsfarm.unipd.it/Lezioni/PSF/PDF/AGuidetoMM&QM.pdf (Dec. 02, 2019).

J. H. Warren, O. Sean, Spartan’16 for Windows, Macintosh and Linux: Tutorial and User Guide, Wavefunction, Irvine, CA, USA, 2017, URL: https://downloads.wavefun.com/Spartan16Manual.pdf (Dec. 02, 2019).

T. Otroschenko, G. Jiang, V. A. Kondratenko, U. Rodemerck, E. V. Kondratenko, Current status and perspectives in oxidative, non-oxidative and CO2-mediated dehydrogenation of propane and isobutane over metal oxide catalysts, Chem. Soc. Rev. 50 (2021) 486–489, doi: https://doi.org/10.1039/d0cs01140a.

S. M. Al-Zahrahi, Propane oxydehydrogenation to propylene over molybdenum-based catalysts. JKSUES 16 (2) (2004) 203–213, doi: https://doi.org/10.1016/S1018-3639(18)30787-6.

M. S. Guzmán1, Y. E. Licea-Fonseca, A. E. Isaza1, A. Faro, L. A. Palacio-Santos, Propylene oxydehydrogenation to propylene over molybdenum-based catalysts, Redin 84 (2017) 97–104, doi: https://doi.org/10.17533/udea.redin.n84a11.

G. A. Shallangwa, A. Uzairu, V. O. Ajibola, H. Abba, DFT and PM3 Computational Studies of the Reaction Mechanism of the Oxidation of L-Tyrosine by Iodine in the Gas Phase, AIJST 3 (2) (2014) 106–115, doi: https://doi.org/10.13170/AIJST.0302.06.