# Modelling of Metal Oxide films for catalytic activity on n-heptane

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## 1. Introduction

Catalysis and adsorption are at the heart of many modern industrial and environmental technologies such as fuel refining, pharmaceutical synthesis, and pollution control. Catalysts lower the activation energy of chemical reactions, enabling them to proceed more rapidly and efficiently, while also enhancing product selectivity and minimizing unwanted by-products [1]. These improvements lead to lower energy consumption and higher process sustainability [2]. A key factor influencing catalytic activity is adsorption: the initial step of catalytic reactions is the attachment of reactant molecules to the catalyst surface. Adsorption may occur through physisorption or chemisorption, depending on the strength and type of surface interactions, and is influenced by surface structure, porosity, and energy profiles [3]. In catalytic systems, optimizing adsorption behaviour is vital for maximizing reaction rates and selectivity.

Metal oxides such as aluminium oxide ($Al_2O_3$) and copper oxide (CuO) have gained attention as promising heterogeneous catalysts due to their low toxicity, thermal stability, and tuneable electronic properties [4]. These materials are widely studied for reactions involving hydrocarbon transformations, including the catalytic conversion of n-heptane, a key compound for simulating hydrocarbon behaviour in refining processes [5]. Understanding how such molecules interact with metal oxide surfaces helps identify active sites, optimize configurations, and improve catalyst performance. In order to probe these interactions at the atomic scale, Molecular Dynamics (MD) simulations are used to enable dynamic visualization and analysis of how molecules behave on surfaces over time, revealing information about adsorption energies, molecular orientations, and diffusion mechanisms [6]. This is especially useful for investigating how variations in catalyst surfaces influence bonding strength and geometry, which are otherwise difficult to capture through an experimental approach alone [7].

In this study, we aim to develop a computational screening method for catalytic materials. Using Material Studio software and MD simulations, we explore the interaction of n-heptane with $Al_2O_3$ and CuO surfaces. Each catalyst is analysed across three molecular orientations to assess adsorption energy, surface bonding configurations, and centroid distances from the surface. We further evaluate the toxicity and economic feasibility of each material to determine the most efficient and sustainable catalytic candidates.

## 2. Aim(s) of the experiment

This study aims to explore the adsorption of n-heptane on two different catalytic systems, in particular to:

- Identify two catalytic systems and define the suitable thickness and slab size by increasing the dimensions of the slabs.
- Compute the bonding energies and adsorption energies of n-heptane on the chosen catalytic surfaces for different molecular orientations.
- Compare the mean values of the optimized data by computing the goal function.

## 3. Experimental section

All modelling and simulations were operated using *Material Studio*, the Forcite module was used for geometry optimization, energy calculations, and Molecular Dynamics (MD) simulations.

The COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field was employed configured as follows:

- **Quality:** Medium
- **Electrostatics:** Ewald summation method
- **Van der Waals (vdW):** Atom-based summation method

The settings were selected in order to achieve a compromise between computational efficiency and simulation precision. The Ewald summation method was chosen for accurately calculating long-range electrostatic interactions, while the atom-based summation method was used to evaluate van der Waals forces.

The *n*-heptane molecule was modelled and optimized to ensure a stable configuration. For each metal oxide system, the following steps were carried out:

1. The unit cell of each metal oxide crystal was constructed.
2. The crystal surface was cleaved along the selected Miller plane of interest to expose the active catalytic face.
3. A supercell was generated by expanding the unit cell in different sizes (2×2, 3×3, 4×4, 5×5, and 6×6) to study the effect of surface area and to minimize edge effects
4. The optimized *n*-heptane molecule was placed above the metal oxide surface in three different orientations to simulate multiple possible adsorption and bonding configurations, and calculated using the following formula below.

$$E_{bonding} = E^{OPT}_{adsorbent+molecule} - (E_{adsorbent}\text{-}E_{molecule})$$

$$E_{adsorption} = E^{OPT}_{adsorbent+molecule} - (E^{OPT}_{adsorbent}\text{-}E^{OPT}_{molecule})$$

5. The crystal surface atoms were constrained, and geometry optimization was performed to minimize the total system energy.
6. To calculate accurate adsorption energies, energy simulations were conducted separately for the isolated surface slab (without *n*-heptane) and the isolated molecule (after removing it from the surface).
7. Using LD50 values and the industrial price per mT of each oxide, the goal function, shown below was used to depict the relative viability of both oxides.

$$Goal\ function = 0.7\frac{Eb}{\max(Eb)} + 0.1\left(1 - \frac{LD50}{\max(LD50)}\right) + 0.2\left(1 - \frac{Price}{\max(Price)}\right)$$

# 4. Results and discussion

### 4.1 Slab thickness optimization

The calculations to determine the best thickness for the catalytic application of the metal oxides with n-heptane were performed using several slab thicknesses. The idea was to identify the point where the bonding energy values stabilized by plotting the results for each thickness, in theory, this would appear as a plateau or a region where the energy variation becomes minimal. However, after running the calculations multiple times across different thicknesses, we unable to observe a clear stabilization in the bonding energy. Because of this, it was not possible to determine the optimal thickness based on these results.

Despite this, we still needed to define a slab thickness in order to proceed with the rest of the simulations. So, we decided to set it arbitrarily, but based on reasonable criteria. We knew the slab couldn't be too thin, as that would weaken the interaction with the molecule, but it also couldn't be too thick, since deeper layers would no longer contribute meaningfully to the interaction and would only increase the computational cost. For that reason, we chose a thickness of 5 times the unit cell length in the Z direction, a safe middle point that's not too thin to be ineffective, and not too thick to be unnecessarily demanding. While the choice was ultimately arbitrary, it was made to ensure a balanced and practical setup for the following calculations.

### 4.2 $Al_2O_3$ slab size optimization

In this section, the results from the calculations used to optimize the slab size for alumina are presented. For $Al_2O_3$ the (110) facet was used as the most active surface, found from the following source [8]. These include both the adsorption and bonding energy calculations, which were carried out to analyse the interaction between n-heptane and the generated slabs. The goal of these studies is to determine the most suitable slab size that can realistically represent the surface for catalytic activity, helping ensure that the alumina model behaves in a consistent and reliable way

#### 4.2.1 $Al_2O_3$ adsorption energy

Once the correct or most suitable thickness of the slab was determined, the next step was to evaluate how the surface interacts with the heptane molecule, since the main goal is to simulate surface behaviour suitable for catalysis. For this, it was necessary to perform adsorption energy calculations of the heptane molecule on the alumina slab, considering three different orientations: 0°, 90°, and 180° (Fig. 1). These calculations provide insight into how strongly the molecule interacts with the surface, which is directly related to the potential catalytic activity of the material.

As shown in Figure 2, the adsorption energy of the molecule was evaluated across different slab sizes. Ideally, one would expect a "stable" energy value, represented as a plateau in the plot; indicating that the surface properties are no longer significantly affected by further increases in slab size. However, this plateau behaviour is not clearly observed for any of the angles tested. Still, when considering the average adsorption energies across the three orientations, it can be seen that the energy begins to stabilize around the 4x4 slab size, suggesting it is a suitable candidate based on average performance.

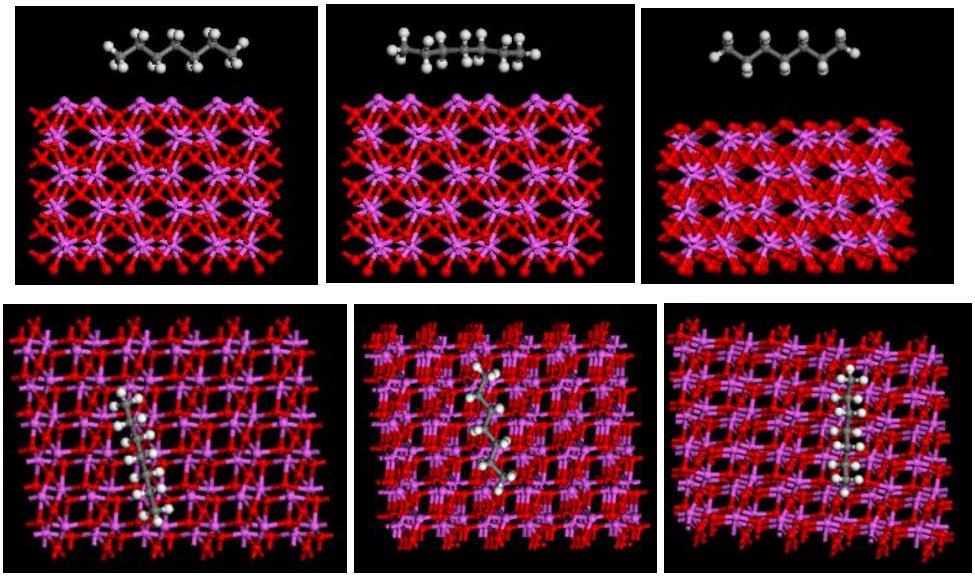

*Figure 1: Visualization of the n-heptane molecule on the $Al_2O_3$ slab in the three different orientations: from left to right: 0°, 90°, and 180°.*

Nevertheless, when analysing the results for each orientation individually, the 3x3 slab size stands out as the point where the adsorption energies for all three angles come closest to stabilizing (lowest values). This is especially relevant because the 90° orientation shows the largest variation in energy across different slab sizes. At the 3x3 size, even this more variable orientation shows improved consistency, by giving the lowest energy value, which supports the idea that this size offers the most balanced and reliable performance overall. Moreover, when analysing the behaviour of the 0° orientation, which is actually the only one that shows a clear plateau, the energy appears to stabilize at the 3x3 slab size. Therefore, considering both the average and the individual behaviours, the 3x3 slab size can be considered the most suitable for further analysis based on adsorption energy. This information is important because it helps make sure the surface we're using in the simulation gives a consistent interaction with the molecule, which is key if we want the catalytic behaviour to be reliable. If the adsorption isn't stable, then any other results we get later might not really reflect how the surface would behave in real conditions. The following section will explore whether this conclusion also holds true when analysing the bonding energy results.

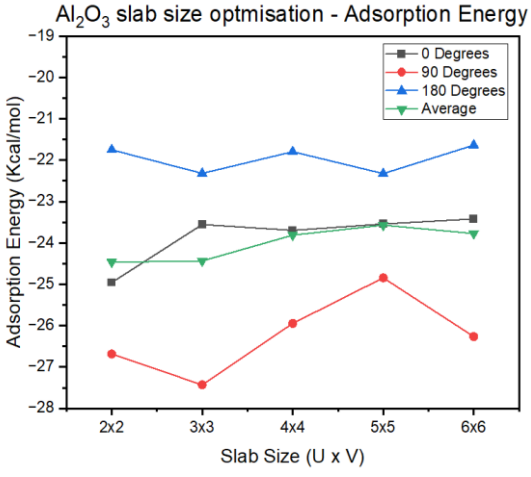


*Figure 2: Plot of adsorption energy versus slab size ($Al_2O_3$) for the three orientations (0°, 90°, and 180°), including the average energy curve.*

### 4.2.2 Al2O3 bonding energy

As was done previously for the adsorption energy, the same set of calculations was carried out using the same slab sizes and molecular orientations (0°, 90°, and 180°; Fig. 1), but this time to determine the bonding energy. Bonding energy is an important parameter when evaluating a potential catalyst because it indicates how strongly the molecule attaches to the surface, not just if it interacts (as in adsorption), but whether it forms a more stable complex that could influence catalytic behavior more directly.

Similar to the adsorption energy results, the bonding energy plot (Fig. 3) does not show a clearly defined plateau. However, in contrast to adsorption, the energies obtained for the different orientations behave more consistently across the tested slab sizes. All three orientations show a more stable and converging trend around the 3x3 slab size, suggesting improved agreement among the angles at this size. And just like in the previous case, the 0° orientation is once again the only one that shows a clear plateau, stabilizing at that slab size. This gives a useful insight to support the idea that this could be the right size to use for the simulation.

The 3x3 slab size is the most suitable for modelling the alumina surface as a catalyst for heptane. The fact that both adsorption and bonding energy calculations point to the same slab size gives stronger confidence in the reliability of this setup. The smoother trend in bonding energy across orientations also suggests that the alumina surface at this size offers a more uniform interaction environment for the heptane molecule, which could be important for designing consistent catalytic performance in real applications.

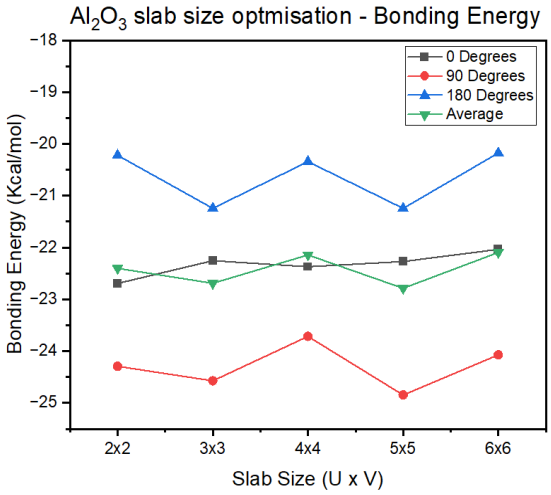


*Figure 3: Plot of bonding energy versus slab size ($Al_2O_3$) for the three orientations (0°, 90°, and 180°), including the average energy curve.*

### 4.2.3 Adsorption and bonding energy characteristics

After analyzing the plots for both adsorption and bonding energies to determine the most suitable slab size, the next step is to take a closer look at the specific energy values and the distance between the slab and the molecule for the selected 3x3 slab. In Table 1, we can see the set of values obtained for this optimized slab. As shown, the 90° orientation gave the most negative values for both adsorption and bonding energies, indicating the strongest interaction between the molecule and the surface. This suggests that 90° is likely the most favorable orientation for catalytic activity. Supporting this, it also shows the smallest distance between the molecule and the slab, which makes sense since a stronger interaction usually leads to a closer approach.

However, this doesn't mean that the other orientations are not suitable. When looking at the average values, the differences between the three angles are not that significant. The standard deviation is 1.3943 for the bonding energy and 2.1769 for the adsorption energy, which shows that while 90° stands out, the energy values across orientations are still in a relatively close range. The same goes for the distances, the average is quite close to each individual orientation, with a small standard deviation of 0.1359, suggesting that the molecule maintains a fairly consistent interaction with the surface regardless of its angle.

Overall, the 90° orientation shows the strongest interaction and would be considered the most favorable, while the 180° orientation appears to be the weakest, showing the highest energy values and the largest distance, both pointing to a less efficient interaction for catalytic purposes.

*Table 1: Bonding and adsorption energies for n-Heptane on $Al_2O_3$ surface for optimised slab size 3x3*

| Optimal slab size | n-heptane orientation [°] | Bonding energy [kcal/mol] | Adsorption energy [kcal/mol] | Distance (Angstroms) |
|---|---|---|---|---|
| 3x3 | 0 | -22.252908 | -23.556431 | 3.443 |
| | 90 | -24.573126 | -27.431344 | 3.376 |
| | 180 | -21.242659 | -22.321435 | 3.692 |
| **Average** | | -22.689564 | -24.436403 | 3.503666667 |
| **Standard Deviation** | | 1.394275 | 2.17693301 | 0.135951789 |

### 4.3 CuO slab size optimization

For CuO we used the (001) as the most active surface, found from the following source [9]. The slab thickness was chosen to converge the adsorption energy (we observed convergence by ~5 CuO layers and ~30 Å vacuum). To determine the most appropriate slab dimensions for modelling the CuO surface, we evaluated five different lateral supercell sizes: 2×2, 3×3, 4×4, 5×5, and 6×6. For each slab size, n-heptane was placed on the surface in three orientations: 0°, 90°, and 180°, and both bonding and adsorption energies were calculated.

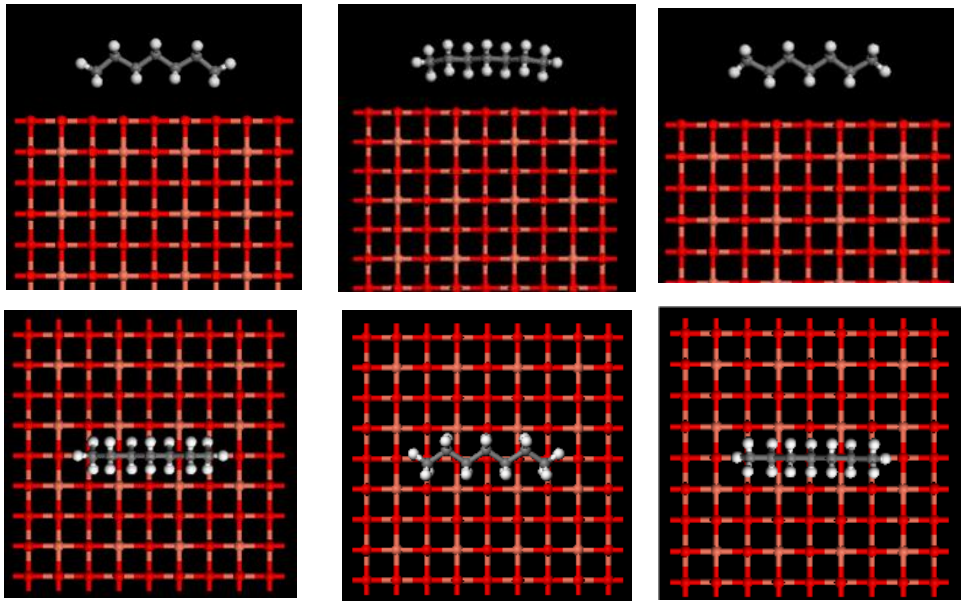

*Figure 4: Visualization of the n-heptane molecule on the CuO slab in the three different orientations: from left to right: 0°, 90°, and 180°.*

### 4.3.1 CuO adsorption energy

From 2×2 to 4×4, adsorption energies improved substantially, with the average increasing from –12.23 kcal/mol to –13.66 kcal/mol. Beyond the 4×4 size, adsorption energies for 5×5 and 6×6 showed minimal improvement, with values of –13.43 and –14.14 kcal/mol, respectively (Fig. 5).

Within the 4×4 slab, the 90° orientation again demonstrated the most favourable adsorption energy, followed by 0° and 180°. The small standard deviation suggests that orientation has a measurable but not drastic effect on adsorption thermodynamics, as mentioned in Table 2.

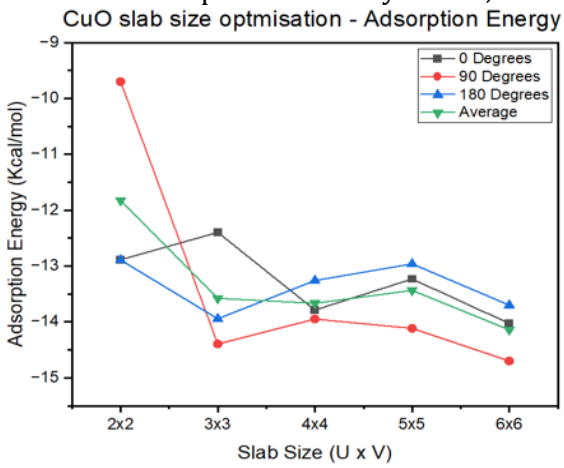


*Figure 5: Plot of adsorption energy versus slab size (CuO) for the three orientations (0°, 90°, and 180°), including the average energy curve.*

### 4.3.2 CuO bonding energy

The bonding energy represents the interaction strength between the n-heptane molecule and the CuO surface without accounting for geometric rearrangement of the molecule. The bonding energy showed an improving trend from 2×2 to 4×4, suggesting stronger molecule-surface interactions with increasing slab size. Beyond the 4×4 slab, additional gains were minimal: 5×5 and 6×6 gave average bonding energies of –12.85 and –13.39 kcal/mol, respectively (Fig. 6).

The 4×4 slab size provides a good compromise between accuracy and computational efficiency. Within the 4×4 system, the most favourable orientation was 90°, with the lowest bonding energy of –13.3788 kcal/mol. The 180° orientation exhibited the weakest interaction at –12.6492 kcal/mol. The standard deviation across orientations was ±0.3172 kcal/mol, suggesting modest orientation dependence, as shown in Table 2.

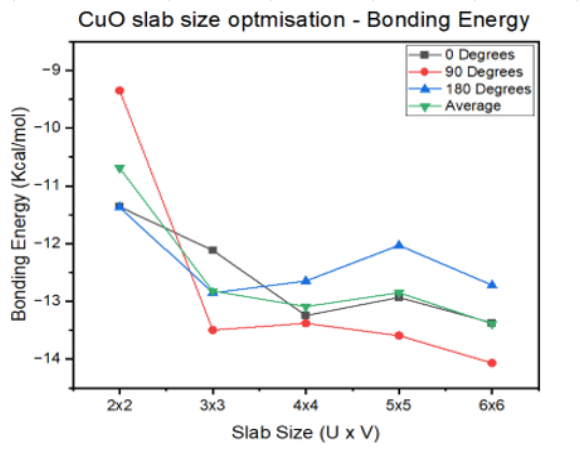


*Figure 6: Plot of adsorption energy versus slab size ($Al_2O_3$) for the three orientations (0°, 90°, and 180°), including the average energy curve.*

*Table 2: Bonding and Adsorption energies for n-Heptane on CuO surface for optimised slab size 4x4*

| Optimal slab size | n-heptane orientation [°] | Bonding energy [kcal/mol] | Adsorption energy [kcal/mol] | Distance (Angstroms) |
|---|---|---|---|---|
| 4x4 | 0 | -13.245447 | -13.786644 | 3.64 |
| | 90 | -13.378846 | -13.947698 | 3.541 |
| | 180 | -12.649164 | -13.258511 | 3.806 |
| **Average** | | -13.0911523 | -13.664284 | 3.662333333 |
| **Standard Deviation** | | 0.31724238 | 0.29436213 | 0.109332317 |

### 4.4 Goal function

*Table 3: Goal function calculation for both oxides with prices and LD50 values*

| Catalyst | Average Eb | SD of Eb | LD50 (mg/Kg) | Price USD$ per metric tonne (mT) | Goal Function |
|---|---|---|---|---|---|
| CuO | -13.091152 | 0.317242 | 470 [10] | 5850 [11] | 0.494478 |
| $Al_2O_3$ | -22.689564 | 1.394275 | 5000 [12] | 366 [13] | 0.887487 |

Table 3 presents the key data obtained from the Molecular Dynamics (MD) simulations and the compiled database. The comparison of goal function values, calculated from Eq. 2, between CuO and $Al_2O_3$ clearly indicates that $Al_2O_3$ is the more favourable catalyst overall. With a goal function score of 0.8875 compared to CuO's 0.4945, $Al_2O_3$ significantly outperforms CuO by nearly a factor of two. This is primarily due to its substantially stronger average bonding energy, indicating more effective adsorption of n-heptane. Additionally, $Al_2O_3$ offers clear advantages in both safety and cost: it has a higher LD50, reflecting lower toxicity, and its price is dramatically lower at only $366 per metric tonne compared to CuO's $5850. These combined factors—stronger interaction with the adsorbate, lower health risk, and greater affordability—result in $Al_2O_3$ achieving a markedly higher goal function score, making it the superior catalyst choice under the given evaluation criteria.

## 4. Conclusions

This study explores the adsorption properties of n-heptane on two different catalytic surface candidates: $Al_2O_3$ and CuO. For $Al_2O_3$, the 3x3 slab size showed to be the most suitable one, in particular at 90°inclination, as it registered the lower value in both the adsorption and bonding energy and lower distance, ultimately showcasing a better interaction overall. CuO showed a similar behaviour at the 4x4 slab size, with similar trends but overall weaker interactions compared to the $Al_2O_3$.

A goal function analysis, taking in account Bonding Energy, toxicity and cost per mT, confirms $Al_2O_3$ as a better catalyst overall scoring 0.887 over the inferior 0.494 of the CuO counterpart.

Overall, this work shows that Computational Modelling is an efficient method to optimise the prediction of catalytic properties of such complex systems, with $Al_2O_3$ emerging as a promising candidate per n-heptane adsorption applications.

# Literature

[1] A. G. H. I. &. L. i. X. F. X. Corma, "Engineering metal organic frameworks for heterogeneous catalysis," *Chemical reviews,* pp. 110(8), 4606-4655, 2010.

[2] A. L. J. &. Z. T. Wang, "Heterogeneous single-atom catalysis," *Nature Reviews Chemistry,* pp. 65-81, 2018.

[3] L. Q. S. W. X. C. X. C. B. &. X. H. Yang, "Energy-efficient separation alternatives: metal–organic frameworks and membranes for hydrocarbon separation," *Chemical Society Reviews,* pp. 49(15), 5359-5406, 2020.

[4] C. B. a. A. I. a. B. E. a. S. V. N. Anucha, "Titanium dioxide ($TiO_2$)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs) degradation: In the light of modification strategies," *Chemical Engineering Journal Advances,* vol. 10, p. 100262, 2022.

[5] A. T. G. A. H. &. A. A. Tanimu, "Catalytic cracking of crude oil: mini review of catalyst formulations for enhanced selectivity to light olefins," *Energy & Fuels,* vol. 36(10), pp. 5152-5166, 2022.

[6] G. L. M. S. Y. S. F. Z. D. C. G. K. L. .. &. R. R. Piccini, "Ab initio molecular dynamics with enhanced sampling in heterogeneous catalysis," *Catalysis Science & Technology,* vol. 12(1), pp. 12-37, 2022.

[7] A. G. a. A.-M. N. a. I. Z. a. Y. R. a. R. S. Z. a. M. N. a. I. A. a. S. S. a. T.-Y. Y. H. Alsultan, "A short review on catalyst, feedstock, modernised process, current state and challenges on biodiesel production," *Alsultan, Abdulkareem G and Asikin-Mijan, Nurul and Ibrahim, Zueriani and Yunus, Robiah and Razali, Siti Zulaika and Mansir, Nasar and Islam, Aminul and Seenivasagam, Sivasangar and Taufiq-Yap, Yun Hin,* vol. 11, p. 1261, 2021.

[8] A. Cholach, "Catalytic activity of γ-Al2O3(110) in the NO + H2 reaction: a DFT study," *Phys. Chem. Chem. Phys.,* vol. 25, no. 36, pp. 24686-24695, 2023.

[9] Z.-Z. D. F. S. Y.-T. J. T.-T. D. C. L. X. Z. Tong Li, "Facet-dependent peroxymonosulfate activity and mechanism of CuO for degradation of organic pollutants," *Journal of Environmental Chemical Engineering,* vol. 12, no. 2, 2024.

[10] N. C. f. B. I. (2025), "PubChem Compound Summary for CID 164827, Cupric Oxide.," 2025. [Online]. Available: https://pubchem.ncbi.nlm.nih.gov/compound/Cupric-Oxide. [Accessed 07 07 2025].

[11] "Copper Oxide Prices Worldwide," Intratec, 05 2020. [Online]. Available: https://www.intratec.us/solutions/primary-commodity-prices/commodity/copper-oxide-prices. [Accessed 07 07 2025].

[12] N. C. f. B. Information, "PubChem Compound Summary for CID 9989226, Aluminum Oxide.," 2025. [Online]. Available: https://pubchem.ncbi.nlm.nih.gov/compound/aluminum%20oxide#section=Non-Human-Toxicity-Excerpts. [Accessed 07 07 2025].

[13] "Aluminum Oxide Prices Worldwide," Intratec, 05 2020. [Online]. Available: https://www.intratec.us/solutions/primary-commodity-prices/commodity/aluminum-oxide-prices. [Accessed 07 07 2025].