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Kinetic Modeling of Methylcyclohexane Dehydrogenation Reaction for Toluene Production in the Polymer Industry

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Abstract

Toluene, also known as methylbenzene, plays an important role in various industries, particularly the polymer industry where it is used as a solvent, an adhesive in resins and an additive in rubber and cosmetic products. However, the current production of toluene in Indonesia is insufficient to meet the growing demand, particularly in the polymer sector, prompting the exploration of alternative production methods. This work investigates the production of toluene through the dehydrogenation of methylcyclohexane (MCH) using a Pt/Al_2O_3 catalyst, a process that also generates hydrogen, contributing to clean energy initiatives. The research focuses on identifying the optimal kinetic model for the dehydrogenation reaction, taking into account reactor design and catalyst performance. Four kinetic models were analysed using Polymath software, with the second model highlighting methylcyclohexane adsorption as the key factor and showing the best agreement with experimental data. The results indicate that toluene production can be improved using a fixed bed reactor and Pt/Al_2O_3 catalyst, with surface reactions as the rate-limiting step, offering promising prospects for meeting the needs of the polymer industry.

Keywords: *toluene, methylcyclohexane, dehydrogenation, Pt/Al_2O_3 catalyst, kinetic model, hydrogen production, clean energy.*

Abstrak

Toluena, atau metilbenzena, memiliki peran penting dalam berbagai industri, terutama dalam industri polimer, di mana ia digunakan sebagai pelarut, perekat dalam resin, serta aditif dalam produk karet dan kosmetik. Namun, produksi toluena di Indonesia saat ini belum mencukupi untuk memenuhi permintaan yang terus meningkat, khususnya di sektor polimer, sehingga diperlukan eksplorasi metode produksi alternatif. Penelitian ini menyelidiki produksi toluena melalui proses dehidrogenasi metilsikloheksana (MCH) menggunakan katalis Pt/Al_2O_3, yang juga menghasilkan hidrogen dan mendukung inisiatif energi bersih. Fokus penelitian ini adalah pada pemilihan model kinetika reaksi yang optimal untuk proses dehidrogenasi, dengan mempertimbangkan desain reaktor dan kinerja katalis. Empat model kinetika dianalisis menggunakan perangkat lunak Polymath, dan model kedua, yang menyoroti adsorpsi metilsikloheksana sebagai faktor utama, menunjukkan kesesuaian terbaik dengan data eksperimen. Hasil penelitian menunjukkan bahwa produksi toluena dapat dioptimalkan melalui penggunaan reaktor fixed-bed dan katalis Pt/Al_2O_3, dengan reaksi permukaan sebagai langkah penentu laju, memberikan prospek yang menjanjikan untuk memenuhi kebutuhan industri polimer.

Kata Kunci: *toluena, metilsikloheksana, dehidrogenasi, katalis Pt/Al_2O_3, model kinetika, produksi hidrogen, energi bersih*

1. Introduction

Toluene, with the IUPAC name methylbenzene, is one of the most valuable organic compounds in modern industry [1]. It is a colorless, water-insoluble liquid with a distinct odor reminiscent of paint thinners [2]. Chemically, toluene belongs to the aromatic hydrocarbon family and is a derivative of benzene with a methyl group attached to the ring structure. Despite its simplicity, toluene plays a crucial role across various industries, serving as a solvent, raw material, and intermediate product for a wide range of commercial and industrial applications [3].

Toluene's extensive use is closely tied to its chemical properties. In the polymer and plastics industries, toluene serves as a solvent in the production of polymers such as polystyrene and polyurethane and is used in the synthesis of resins and synthetic rubber. Additionally, toluene acts as a precursor in the production of monomers and polymerization materials [4]. Its widespread presence in the polymer industry makes it a key component in the manufacturing processes of various plastic products used in everyday life, such as packaging, automotive components, and electronic devices.

Global demand for toluene continues to rise, particularly in developing countries experiencing rapid industrial growth. In Indonesia, the consumption of toluene has significantly increased over the past decade, largely due to the expansion of the plastics and polymer sectors [5]. However, local production has not been able to keep up with this demand. Indonesia relies heavily on imports to meet its industrial needs, particularly in the polymer and plastics sectors. In 2015, Indonesia imported 108,302 tons of toluene, valued at USD 78.8 million, and this figure increased to 119,901 tons, worth USD 76.6 million in 2016 [6]. These figures highlight the urgent need for the country to explore alternative methods to boost local toluene production, especially to meet the demands of the polymer and plastics industries.

Traditionally, toluene is produced from crude oil, particularly from naphtha, through a process called catalytic reforming [7]. However, this method is heavily dependent on crude oil, and with growing environmental concerns and the push for cleaner energy sources, alternative production methods are gaining attention. One promising method for producing toluene is the dehydrogenation of methylcyclohexane (MCH), which is also derived from naphtha [8]. This reaction not only produces toluene but also generates hydrogen, which can be used as a clean energy source.

This research aims to investigate the dehydrogenation of methylcyclohexane in the production of toluene and hydrogen, with a focus on its application in the polymer and plastics industries. The main areas of study include identifying optimal catalysts, analyzing reaction mechanisms, and determining the most suitable kinetic models to describe the reaction. Additionally, the research will explore the operational conditions under which the reaction is most efficient, such as temperature, pressure, and appropriate reactor design, with the goal of providing a comprehensive framework for enhancing toluene production to support the growth of Indonesia’s polymer industry.

The research will also consider industrial challenges, such as catalyst deactivation and scaling issues. The fixed-bed reactor design, which is effective for high-temperature and high-pressure reactions, will be evaluated as an ideal choice for the dehydrogenation of methylcyclohexane within the context of the polymer and plastics industries.

With the increasing demand for toluene in the polymer and plastics industries, along with the importance of hydrogen as a clean energy source, this research will provide valuable insights into the kinetics and mechanisms of the reaction, supporting the development of more efficient and sustainable methods for toluene and hydrogen production.

2. Material and Methods

Materials

The primary material, methylcyclohexane (MCH), was selected for its structural similarity to toluene, with the chemical formula $CH_3C_6H_{11}$. MCH is a colorless, flammable liquid with a boiling point of 101°C, typically derived from naphtha. This compound was chosen due to its ability to undergo dehydrogenation, which involves the removal of hydrogen atoms from the molecule, converting it into toluene [9]. MCH serves as the hydrogenated form of toluene, and its high reactivity makes it an ideal candidate for this chemical process.

To facilitate the dehydrogenation reaction, a platinum-based catalyst (Pt/Al_2O_3) was employed. Platinum (Pt) was selected as the active catalytic material because of its efficiency in breaking C-H and H-H bonds, essential steps in the dehydrogenation process [10]. The platinum was supported on aluminum oxide (Al_2O_3), chosen for its large surface area and high thermal stability, which are crucial for maintaining catalyst performance at elevated temperatures [11]. The catalyst was prepared with 1.0 wt% platinum on Al_2O_3, which was determined to provide optimal catalytic performance based on prior studies. This preparation involved impregnation, drying, calcination, and reduction processes to activate the platinum particles and make them effective for the reaction.

Experimental Setup

The dehydrogenation of methylcyclohexane was performed using a fixed-bed reactor, which was selected for its efficiency in managing high-temperature and high-pressure reactions [12]. The fixed-bed design was particularly suited for this study, as it allows for effective interaction between the gas-phase reactants and the solid catalyst. This type of reactor provides a controlled environment where the reactants can flow over the catalyst bed, enabling optimal reaction conditions.

The reactor was constructed from stainless steel (SS-316), a material chosen for its durability and high resistance to the extreme temperatures and pressures required for the dehydrogenation process [13]. Stainless steel ensures that the reactor can operate for extended periods without degrading or reacting with the chemicals involved. The reactor’s design was carefully tailored to suit the experiment’s needs, with a tube length of 66 cm and a reactor bed length of 55 cm. These dimensions provided ample space for the catalyst and the reactants to interact efficiently. The tube's internal diameter of 1.02 cm and external diameter of 1.27 cm ensured a smooth flow of reactants, minimizing pressure drop and maximizing contact with the catalyst surface.

To ensure precise control over the temperature within the reactor, a thermowell made from aluminum oxide (Al_2O_3) was integrated into the setup. The thermowell, with an external diameter ranging from 0.2880 cm to 0.3175 cm, allowed accurate temperature monitoring during the reaction process. This was crucial, as maintaining the correct temperature is key to the success of the dehydrogenation reaction. The use of Al_2O_3 for the thermowell added to the system's stability, as it can withstand high temperatures without degrading or influencing the reaction.

Reaction Conditions

The dehydrogenation reaction of methylcyclohexane to produce toluene was conducted under carefully controlled conditions to ensure the efficiency and stability of the process. The temperature of the reaction was maintained within a range of 315°C to 372°C, a range determined through previous studies to provide the optimal environment for the Pt/Al_2O_3 catalyst to function effectively. This temperature range was essential in ensuring the correct activation of the catalyst and promoting the dehydrogenation process while avoiding any thermal degradation of the reactants or the catalyst itself [14].

In addition to temperature control, the pressure within the reactor was carefully regulated. The total pressure was kept between 1.42 bar and 6.38 bar, providing the necessary conditions for the reaction to proceed smoothly. Maintaining this pressure range ensured that the dehydrogenation process remained stable and efficient without causing excessive stress on the catalyst, which could lead to deactivation or unwanted side reactions [15].

The feed composition was also meticulously managed. The only reactant introduced into the reactor was liquid methylcyclohexane, which was fed at a controlled rate to ensure a steady-state condition throughout the reaction process. By controlling the feed rate, the experiment minimized the likelihood of fluctuations in reactant concentration, which could otherwise lead to inconsistent reaction rates or cause the catalyst to deactivate prematurely. This steady-state approach allowed for precise and reliable data collection while optimizing the overall efficiency of the reaction [16].

Catalyst Preparation

The preparation of the Pt/Al_2O_3 catalyst was carried out using a method known as impregnation, a widely-used technique in catalyst production due to its ability to ensure uniform distribution of active metal particles [17]. The process began with the creation of a platinum salt solution, which was carefully mixed with aluminum oxide (Al_2O_3) as the support material. The purpose of this step was to allow the platinum particles to disperse evenly across the surface of the Al_2O_3, forming a consistent and effective catalyst.

Once the impregnation process was complete, the catalyst underwent a drying stage at 120°C. This step was essential to remove any remaining moisture or solvent from the catalyst mixture, ensuring that the platinum particles adhered firmly to the surface of the Al_2O_3 [18]. The drying process resulted in a dry powder, with the platinum precursor adsorbed onto the surface of the support material.

Following drying, the catalyst was subjected to calcination at 500°C for a duration of four hours in an air atmosphere. Calcination is a critical step in catalyst preparation, as it decomposes the platinum precursor, leaving behind active platinum particles. This high-temperature treatment also promotes the bonding between platinum and the Al_2O_3 support, increasing the durability and efficiency of the catalyst.

Finally, the catalyst was activated through a reduction process. This involved exposing the catalyst to a flow of hydrogen gas at 400°C for two hours. The reduction stage served to eliminate any residual oxygen or impurities from the surface of the platinum particles, ensuring the catalyst's readiness for the dehydrogenation reaction. Through this series of carefully controlled steps, the Pt/Al_2O_3 catalyst was fully prepared and optimized for use in the reaction process.

Data Analysis

The analysis of the experimental data was performed using Polymath 6.1 software, a tool designed for solving mathematical problems and analyzing data related to chemical reactions. Polymath was instrumental in this study, as it allowed the researchers to accurately process and interpret the experimental data gathered during the dehydrogenation of methylcyclohexane.

By inputting the collected data into the software, Polymath enabled the team to perform non-linear regression analysis, which was essential for comparing the experimental results against the various proposed kinetic models. Through this process, the software calculated key kinetic parameters, such as the reaction rate constants and equilibrium adsorption constants. These parameters were critical in understanding how the dehydrogenation reaction progressed under the given experimental conditions.

The primary objective of this data analysis was to determine which kinetic model provided the best fit for the experimental data. Polymath 6.1 calculated the R^2 value for each model, a statistical measure that indicates how well the model explains the variability of the experimental data. The model with the highest R^2 value was selected as the best representation of the dehydrogenation kinetics, as it demonstrated the closest match between the predicted and observed reaction rates.

Additionally, residual analysis was performed to ensure the chosen model accurately reflected the behavior of the system without significant deviations. By combining R^2 values with residual checks, the data analysis process in Polymath 6.1 ensured a robust and reliable conclusion, providing a clear understanding of the reaction's kinetics and confirming the most accurate model for further optimization.

Safety Considerations

Safety was a top priority throughout the experimental process, given the high temperatures and pressures involved in the dehydrogenation reaction, along with the flammability of the chemicals used, particularly methylcyclohexane and hydrogen. Both substances pose significant risks when subjected to the elevated conditions necessary for this reaction, requiring stringent safety protocols to ensure the protection of both personnel and equipment.

The reactor system was equipped with pressure relief valves to mitigate the risk of over pressurization, which could lead to dangerous system failures. These valves were crucial in maintaining the integrity of the reactor, automatically releasing pressure if it exceeded safe limits. This safeguard ensured that the system could operate safely even under high-pressure conditions.

Additionally, the entire experiment was conducted in a well-ventilated laboratory environment. Proper ventilation was essential to prevent the accumulation of flammable gases like hydrogen, which could lead to explosions if not carefully managed. By ensuring a continuous flow of air throughout the workspace, the risk of gas buildup was significantly reduced, creating a safer environment for conducting high-temperature chemical reactions.

These safety measures were strictly adhered to throughout the study, ensuring that all experimental procedures were carried out in a controlled and secure manner. By prioritizing these protocols, the research team was able to focus on obtaining accurate results without compromising safety.

3. Results and Discussion

In this section, the determination of the reaction rate is discussed based on various kinetic models that describe the dehydrogenation of methylcyclohexane. By evaluating experimental data and testing multiple reaction rate models, the study aims to identify the most accurate model to represent the behavior of the reaction under the given conditions. This analysis is critical for optimizing the production of toluene and improving the overall efficiency of the process.

Selection of Reaction Kinetic Model

Based on the given problem, the author was provided with several reaction rate models. The available reaction rate models are as follows:

$$-r'_M = kP_M^{\alpha} P_{H_2}^{\beta} \tag{1}$$

$$-r'_M = \frac{kP_M}{1 + K_M P_M} \tag{2}$$

$$-r'_M = \frac{kP_M P_{H_2}}{(1 + K_M P_M)^2} \tag{3}$$

$$-r'_M = \frac{kP_M P_{H_2}}{1 + K_M P_M + K_{H_2} P_{H_2}} \tag{4}$$

In addition, the author was given data obtained from experimental results, as shown below:

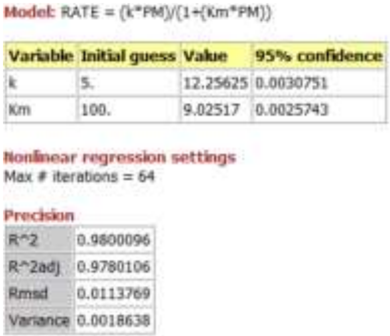
Table 1. Experimental Data for Methylcyclohexane Dehydrogenation

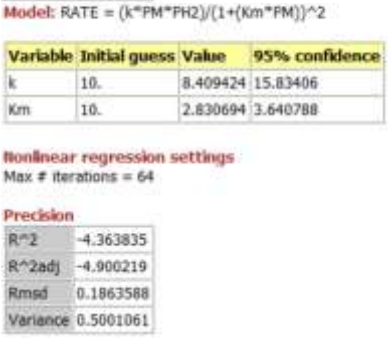
P H_2 (atm)	P M (atm)	r T (mol tolune/s.kg-cat)
1	1	1.2
1.5	1	1.25
0.5	1	1.30
0.5	0.5	1.1
1	0.25	0.92
0.5	0.1	0.64
3	3	1.27
1	4	1.28
3	2	1.25
4	1	1.30
0.5	0.25	0.94
2	0.05	0.41

The author tested each reaction rate model using Polymath 6.1 software to assess the fit between the data and the different reaction rate models. The linearity produced by each reaction rate model was analyzed. Below are the results of Polymath's analysis for each reaction rate model.

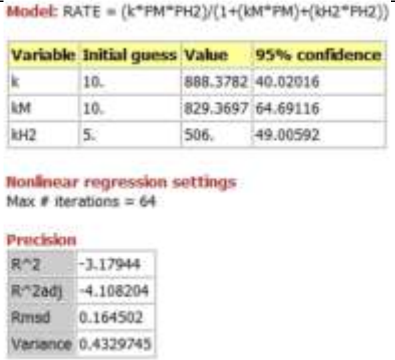
Table 2. Polymath Analysis Results (Non-Linear Regression)

<table>
<tr><th>No</th><th>Model</th><th>Polymath Analysis Results</th></tr>
<tr><td>1</td><td>$-r'_M = kP_M^{\alpha}P_{H_2}^{\beta}$</td><td>
Model: RATE = k*(PH2^a)*(PM^b)
<table>
<tr><th>Variable</th><th>Initial guess</th><th>Value</th><th>95% confidence</th></tr>
<tr><td>k</td><td>10.</td><td>1.148149</td><td>0.1015935</td></tr>
<tr><td>a</td><td>2.</td><td>-0.030869</td><td>0.1217544</td></tr>
<tr><td>b</td><td>2.</td><td>0.1843053</td><td>0.0818913</td></tr>
</table>
Nonlinear regression settings
Max # iterations = 64

Precision
<table>
<tr><td>R^2</td><td>0.7852809</td></tr>
<tr><td>R^2adj</td><td>0.7375655</td></tr>
<tr><td>Rmsd</td><td>0.0372861</td></tr>
<tr><td>Variance</td><td>0.0222441</td></tr>
</table></td></tr>
<tr><td>2</td><td>$-r'_M = \frac{kP_M}{1+K_MP_M}$</td><td>
Model: RATE = (k*PM)/(1+(Km*PM))
<table>
<tr><th>Variable</th><th>Initial guess</th><th>Value</th><th>95% confidence</th></tr>
<tr><td>k</td><td>5.</td><td>12.25625</td><td>0.0030751</td></tr>
<tr><td>Km</td><td>100.</td><td>9.02517</td><td>0.0025743</td></tr>
</table>
Nonlinear regression settings
Max # iterations = 64

Precision
<table>
<tr><td>R^2</td><td>0.9800096</td></tr>
<tr><td>R^2adj</td><td>0.9780106</td></tr>
<tr><td>Rmsd</td><td>0.0113769</td></tr>
<tr><td>Variance</td><td>0.0018638</td></tr>
</table></td></tr>
<tr><td>3</td><td>$-r'_M = \frac{kP_MP_{H_2}}{(1+K_MP_M)^2}$</td><td>
Model: RATE = (k*PM*PH2)/(1+(Km*PM))^2
<table>
<tr><th>Variable</th><th>Initial guess</th><th>Value</th><th>95% confidence</th></tr>
<tr><td>k</td><td>10.</td><td>8.409424</td><td>15.83406</td></tr>
<tr><td>Km</td><td>10.</td><td>2.830694</td><td>3.640788</td></tr>
</table>
Nonlinear regression settings
Max # iterations = 64

Precision
<table>
<tr><td>R^2</td><td>-4.363835</td></tr>
<tr><td>R^2adj</td><td>-4.900219</td></tr>
<tr><td>Rmsd</td><td>0.1863588</td></tr>
<tr><td>Variance</td><td>0.5001061</td></tr>
</table></td></tr>
</table>

No	Model	Polymath Analysis Results
4	$-r'_M = \dfrac{kP_M P_{H_2}}{1 + K_M P_M + K_{H_2} P_{H_2}}$	

Model: RATE = (k*PM*PH2)/(1+(kM*PM)+(kH2*PH2))

Variable	Initial guess	Value	95% confidence
k	10.	888.3782	40.02016
kM	10.	829.3697	64.69116
kH2	5.	506.	49.00592

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	-3.17944
R^2adj	-4.108204
Rmsd	0.164502
Variance	0.4329745

Model 1 assumes that the reaction rate is governed by a power-law relationship with both the partial pressures of methylcyclohexane (P_M) and hydrogen (P_{H2}), with exponents α and β determining the sensitivity of the reaction to changes in these pressures.

The regression results for this model showed a rate constant k of 1.15 with a confidence interval of ± 0.1016, indicating a moderate effect of both P_M and P_{H2} on the reaction rate. The exponent for methylcyclohexane (α) was found to be -0.03, implying a weak and slightly negative impact of P_M on the rate. The exponent for hydrogen (β) was fitted to 0.18, indicating a minor positive influence of P_{H2}.

The precision metrics for this model indicated a relatively poor fit. The R^2 value was 0.785, meaning that approximately 78.5% of the variance in the data could be explained by the model. However, the adjusted R^2 of 0.737 and the relatively high Rmsd of 0.037 suggest that there is still considerable unexplained variability, and the model is not a perfect fit for the data. The variance of 0.0222 further supports this conclusion, indicating a moderate degree of error in the model's predictions.

Model 2 introduces a saturation effect in the reaction rate, where the rate increases with P_M but eventually levels off due to a saturation of the reaction sites. This model focuses solely on the partial pressure of methylcyclohexane and does not directly include P_{H2}.

The fitted values for this model indicated a rate constant k of 12.26 with a narrow confidence interval of ±0.0031, demonstrating high precision. The adsorption constant K_M was fitted to 9.03, with a confidence interval of ±0.0026, suggesting a moderate interaction between methylcyclohexane and the catalyst surface.

Model 2 provided an excellent fit to the experimental data, with an R^2 value of 0.980, meaning that 98% of the variance in the data was explained by the model. The adjusted R^2 was similarly high at 0.978, indicating that the model complexity was well justified. The Rmsd of 0.0114 was low, indicating minimal deviation between the predicted and observed values. The variance of 0.00186 further supports the model's precision, confirming that it provides a highly accurate description of the reaction kinetics.

Model 3 builds on the previous models by incorporating both P_M and P_{H2} in the reaction rate, with a saturation term $(1+ K_M P_M)^2$ in the denominator. This suggests a stronger saturation effect, where increasing P_M suppresses the reaction rate more significantly.

The fitted values for Model 3 indicated a rate constant k of 8.41 with a wide confidence interval of ±15.83, showing considerable uncertainty. The adsorption constant K_M was fitted to 2.83 with a confidence interval of ± 3.64, indicating a weaker interaction between methylcyclohexane and the catalyst than in Model 2.

The performance of Model 3 was poor, with an R^2 value of -4.36, indicating that the model explained virtually none of the variance in the data and performed worse than a simple mean predictor. The adjusted R^2 was even lower at -4.90, highlighting the model's inability to fit the data. The Rmsd was relatively high at 0.186, and the variance was 0.500, both of which indicate significant errors in the model's predictions.

Model 4 adds further complexity by introducing both P_M and P_{H2} in the denominator, each with its own adsorption constant. This model suggests competitive adsorption between methylcyclohexane and hydrogen on the catalyst surface.

The regression analysis yielded a rate constant k of 888.38 with a confidence interval of ±40.02, suggesting that the reaction rate is highly sensitive to reactant concentrations. The adsorption constant for methylcyclohexane K_M was fitted to 829.37, while the adsorption constant for hydrogen K_{H2} was 506.0. Both values were much higher than expected, and their wide confidence intervals suggest significant uncertainty in these estimates.

Model 4 also performed poorly, with an R^2 value of -3.18 and an adjusted R^2 of -4.11, indicating that the model did not fit the data well. The Rmsd was 0.1645, and the variance was 0.4329, both of which indicate substantial errors in the model's predictions. The high fitted values for K_M and K_{H2} suggest overfitting, leading to unrealistic parameter estimates.

In summary, Model 2 provided the best fit to the experimental data, with high R^2 and adjusted R^2 values, low Rmsd, and minimal variance. This model's simplicity and focus on saturation kinetics for methylcyclohexane made it the most accurate in describing the reaction kinetics.

In contrast, Models 3 and 4, which incorporated more complex interactions between P_M and P_{H2}, failed to accurately represent the data. The negative R^2 values and high error metrics for these models suggest that the added complexity did not improve the fit and, in fact, led to poor predictions. Model 1 provided a reasonable fit but was less accurate than Model 2, due to its reliance on a simple power-law relationship, which did not capture the saturation effects as effectively.

Thus, Model 2 is the preferred model for describing the dehydrogenation of methylcyclohexane under the given conditions, offering a balance between accuracy and simplicity.

Selection of Rate Determining Step

To determine the rate-determining step (RDS), a crucial factor in understanding the overall kinetics of a chemical reaction, it is essential to analyze the individual stages of the process in detail. The RDS is the slowest step in the reaction mechanism, effectively controlling the speed of the entire reaction. In the case of methylcyclohexane (MCH) dehydrogenation to toluene (T) and hydrogen (H_2), the reaction can be broken down into distinct steps: adsorption of methylcyclohexane onto the catalyst surface and the surface reaction, where adsorbed methylcyclohexane transforms into products.

By assuming either adsorption or the surface reaction as the rate-determining step, we can derive corresponding rate equations and compare them with experimental data. This comparison allows us to evaluate which step truly governs the reaction's overall rate. In this section, we will delve into the mathematical formulations and conceptual frameworks of both assumptions, linking them to the previously discussed kinetic models and experimental findings. Through this structured analysis, we aim to identify the most likely rate-determining step, thereby improving our understanding of the dehydrogenation process and enhancing the efficiency of the catalytic reaction.

The dehydrogenation of methylcyclohexane is represented by the following reaction:

$$CH_3C_6H_{11} \leftrightarrow CH_3C_6H_5 + 3H_2 \qquad (5)$$

This reaction can be broken down into two primary steps:

1. Adsorption: Methylcyclohexane molecules (M) adsorb onto the catalyst surface (S), forming the complex M.S
   $$M + S \leftrightarrow M.S \qquad (6)$$
2. Surface Reaction: The adsorbed methylcyclohexane (M.S) undergoes dehydrogenation to form toluene (T) and three molecules of hydrogen (H_2), releasing the catalyst surface.
   $$M.S \leftrightarrow T + 3H_2 + S \qquad (7)$$

Assumption 1: Adsorption as the Rate-Determining Step

Under the assumption that adsorption is the rate-determining step (RDS), the rate equation is derived from the adsorption process, considering that the surface reaction occurs rapidly. The rate of adsorption is expressed as:

$$-r_A = k_A\left(P_M C_v - \frac{k'_A C_{M.S}}{k_A}\right) \qquad (8)$$

Where:

- r_A is the rate of adsorption
- k_A and k_A' are the rate constants for the forward and reverse adsorption steps
- P_M is the partial pressure of methylcyclohexane
- C_v is the concentration of vacant sites on the catalyst
- $C_{M.S}$ is the concentration of adsorbed methylcyclohexane

As the surface reaction is assumed to be fast, the surface reaction rate is considered negligible (approaching zero), leading to:

$$-r_p = k_p\left(C_{M.S} - \frac{P_T P_{H_2}^3 C_v}{K_P}\right) \approx 0 \qquad (9)$$

By solving for the concentration of adsorbed species and substituting into the rate equation, the overall rate expression becomes:

$$r_p = \frac{kP_M}{1 + K_M P_M} \tag{10}$$

If adsorption is assumed to be the slowest step in the reaction sequence, it would control the overall reaction rate. In this scenario, the surface reaction is considered to occur rapidly once the methylcyclohexane is adsorbed onto the catalyst surface. The rate equation derived from this assumption emphasizes the competition between the partial pressure of methylcyclohexane (P_M) and the available vacant catalyst sites (C_V)

The adsorption rate equation, shown earlier, assumes that the equilibrium between the adsorbed and free methylcyclohexane molecules is the bottleneck of the reaction. This rate equation suggests that as the partial pressure of methylcyclohexane increases, the reaction rate approaches saturation due to the limited number of vacant catalyst sites. The adsorption step becomes less effective at higher pressures, resulting in a leveling off of the reaction rate, which is consistent with the experimental data.

Assumption 2: Surface Reaction as the Rate-Determining Step

In this scenario, the surface reaction is assumed to be the slowest and thus the rate-determining step. The adsorption process is considered fast, and the rate of the overall reaction is governed by the transformation of adsorbed methylcyclohexane into products. The rate of the surface reaction can be written as:

$$-r_p = k_p \left(C_{M.S} - \frac{P_T P_{H_2}^3 C_v}{K_P} \right) \tag{11}$$

Since the adsorption step is fast, the equilibrium relationship for the adsorbed species is used to express the surface coverage $C_{M.S}$. This leads to the following rate expression for the surface reaction:

$$r_p = \frac{kP_M}{1 + K_P P_M} \tag{12}$$

By comparing the derived rate expressions from both assumptions with the experimentally determined reaction rate expression, it is concluded that the surface reaction is the most likely rate-determining step. This is evidenced by the fact that the final derived rate equation:

$$r_p = \frac{kP_M}{1 + K_M P_M} \tag{13}$$

matches the experimental data closely. Thus, the overall reaction rate is controlled by the transformation of methylcyclohexane on the catalyst surface, with adsorption being a fast, preceding step.

This analysis connects back to the kinetic models discussed earlier, particularly Model 2, which was found to best describe the experimental data. The final rate expression derived here is consistent with the structureof Model 2, reinforcing the conclusion that the surface reaction is the rate-determining step in the dehydrogenation of methylcyclohexane.

If the surface reaction is the slowest and most limiting step, then the overall reaction rate would be dictated by the transformation of adsorbed methylcyclohexane into toluene and hydrogen. In this case, the adsorption process is assumed to be fast, meaning that the concentration of adsorbed species is in equilibrium with the partial pressure of methylcyclohexane.

The rate equation derived from this assumption introduces additional terms for the competition between methylcyclohexane and hydrogen on the catalyst surface. The resulting rate equation also takes the form of a saturation-type kinetic model, but with more emphasis on the equilibrium between the adsorbed species and the gas-phase products.

Assumption 2 is chosen as the more accurate representation of the rate-determining step because the rate equation derived from this assumption closely matches the experimentally observed rate behavior. The kinetic model under this assumption explains the saturation of the reaction rate at higher methylcyclohexane pressures, which was confirmed by the experimental data. At low pressures, the reaction rate increases significantly, but at higher pressures, the reaction begins to saturate, consistent with the surface reaction being the slowest and most limiting step in the process.

The results from Model 2, which was derived from this assumption, show that it provides the best fit to the experimental data compared to the other models tested. Model 2 accurately captures the saturation effect at higher MCH pressures, supporting the conclusion that the surface reaction is the rate-determining step. The match between the derived rate equation and the experimental data reinforces that the overall reaction is controlled by the transformation of methylcyclohexane on the catalyst surface, rather than the adsorption process.

Thus, Assumption 2 better describes the overall reaction kinetics, making it the more suitable choice for understanding and optimizing the dehydrogenation process. By identifying the surface reaction as the rate-determining step, efforts to improve the reaction efficiency can focus on enhancing the catalytic surface reaction, such as by increasing catalyst activity or improving the desorption of products like toluene and hydrogen from the catalyst surface.

4. Conclusion

This study focused on the dehydrogenation of methylcyclohexane (MCH) to produce toluene (T) and hydrogen (H_2), investigating the reaction kinetics and determining the rate-determining step (RDS) of the process. By testing several kinetic models and analyzing both the adsorption and surface reaction mechanisms, we were able to identify the key factors controlling the overall reaction rate.

The kinetic analysis revealed that Model 2, which assumes that the surface reaction is the rate-determining step, provided the best fit to the experimental data. This model accurately captured the behavior of the reaction, especially the saturation effect observed at higher methylcyclohexane pressures. The derived rate equation from this assumption closely matched the experimental findings, confirming that the transformation of adsorbed methylcyclohexane into toluene and hydrogen on the catalyst surface is the slowest and limiting step.

By identifying the surface reaction as the RDS, this research highlights the importance of improving catalytic activity and optimizing surface reaction conditions to enhance the overall efficiency of the dehydrogenation process. Strategies such as increasing catalyst surface area, improving product desorption, or utilizing more active catalytic materials could further accelerate the reaction and improve yields.

In conclusion, this study provides a comprehensive understanding of the reaction kinetics of methylcyclohexane dehydrogenation and offers valuable insights into optimizing the process for industrial applications. By focusing on the surface reaction as the rate-limiting step, future efforts can be directed toward improving catalyst performance and reaction efficiency.

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6. Abbreviations

MCH	Methylcyclohexane
T	Toluene
H_2	Hydrogen
RDS	Rate-Determining Step
Pt/Al_2O_3	Platinum on Aluminum Oxide Catalyst
P_M	Partial Pressure of Methylcyclohexane
P_{H2}	Partial Pressure of Hydrogen
K_M	Adsorption Equilibrium Constant for Methylcyclohexane
K_P	Adsorption Equilibrium Constant for Products
C_V	Concentration of Vacant Sites on Catalyst
$C_{M.S}$	Concentration of Adsorbed Methylcyclohexane
r_A	Rate of Adsorption
r_P	Rate of Surface Reaction
k_A	Rate Constant for Adsorption
k_P	Rate Constant for Surface Reaction

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