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# Methylcyclohexane Dehydrogenation over Commercial 0.3 Wt% Pt/Al$_2$O$_3$ Catalyst

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**Abstract:** Dehydrogenation of methylcyclohexane is studied over commercial 0.3 wt% Pt/Al$_2$O$_3$ catalyst. The effect of catalyst particle size, space velocity, temperature, and partial pressure of hydrogen was studied. It was observed that the dehydrogenation reaction is a strong function of the ratio of reactor internal diameter to catalyst particle size, temperature, and feed composition. The experimental data obtained was kinetically analyzed and first order power law model considering reversible reaction was found appropriate. The apparent activation energy of the catalyst was 100.6 kJ/mol.

## INTRODUCTION

The three most important reasons for studying the dehydrogenation reaction are: a) exploiting methylcyclohexane (MCH) as a fuel; b) investigating the MCH dehydrogenation model reforming reaction; and c) the potential of MCH as a hydrogen energy storage material [1]. As a hydrogen storage energy material, MCH is exploited in the MTH (methylcyclohexane-toluene-hydrogen)-system [2-7]. The MTH-system is a safe and efficient means of storage and "on-board" hydrogen generation. The dehydrogenation reactor installed within the vehicle itself produces hydrogen (see Eq. 1), which can either be used in a spark-ignition engine or in a fuel cell stack. The products of dehydrogenation reaction are cooled and toluene is condensed and separated *in situ*. At the filling station, toluene is pumped out while methylcyclohexane is pumped into the vehicle. Toluene is transported to the hydrogenation plant where it is hydrogenated back to methylcyclohexane (Eq. 2). Hydrogen required for the hydrogenation is produced from a sustainable energy source, such as solar, wind, wave, or even nuclear power. The heart of the MTH-system is the dehydrogenation reaction. An efficient dehydrogenation catalyst is required that is highly active, highly selective towards toluene, and stable over an extended period of time. Established commercial catalyst is ideally suited and can be readily incorporated to obtain reaction data for design and development of practical reactors. This approach saves time, effort, and cost associated with the development of a new catalyst. In the literature, there is a massive controversy among researchers over the kinetics of the dehydrogenation reaction. A wide range of apparent activation energy values are reported, ranging from 17.6 kJ/mol [8] to 220.7 kJ/mol [9]. Therefore, it was thought worthwhile to test a commercial catalyst and to study the kinetics of the reaction. In this study, a commercial dehydrogenation catalyst was studied for methylcyclohexane dehydrogenation. The dehydrogenation reaction was studied for varying particle size and space times at different temperatures both with and without hydrogen addition in the feed. The data so obtained was analyzed numerically and a kinetic model is proposed for the catalytic reaction following the reaction sequence:

Forward Reaction:

$$\underset{\textit{MCH}}{C_7H_{14}} \xrightarrow{+\ \text{Heat}} \underset{\textit{Toluene}}{C_7H_8} + 3\ H_2 \quad (+\,\Delta h^{\circ}_{rxn} = 205\ \text{kJ/mol}) \qquad (1)$$

Reverse Reaction:

$$\underset{\textit{Toluene}}{C_7H_8 + 3\ H_2} \xrightarrow{-\ \text{Heat}} \underset{\textit{MCH}}{C_7H_{14}} \quad (-\,\Delta h^{\circ}_{rxn} = 205\ \text{kJ/mol}) \qquad (2)$$

## MATERIALS AND METHODS

The experimental setup, shown in Fig. 1, mainly consisted of a 11.2 mm I.D. glass fixed bed tubular reactor, a three zone furnace to maintain uniform reactor wall temperature, cooler-condenser operated on glycol refrigeration

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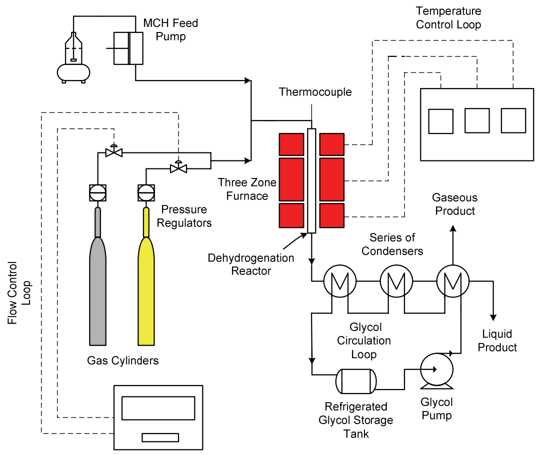

**Fig. 1.** Experimental setup for studying the dehydrogenation reaction of methylcyclohexane.

system, an HPLC feed pump and instruments to measure and control the required process variables. Specifications of the reactor assembly are given in Table 1. The catalyst employed was commercial 0.3 wt% $Pt/Al_2O_3$. This was the only information provided by the supplier and no further attempt was made to characterize the catalyst. However, visual inspection of the catalyst cross-section reveals that the catalyst is an “egg-shell” type. As received, the catalyst was spherical shaped 1.5 to 2.0 mm (1.75 mm average) diameter. The catalyst was used as supplied in a spherical form, catalyst was halved and cut to quarter portions of the original catalyst size. Experiments were performed for three different reactor internal diameters to catalyst particle ratios (24.0, 36.0, and 72.0). Internal diameter of the reactor is the equivalent diameter of the annular region between the reactor tube and thermowell, while catalyst particle size is the nominal particle size, $d_{vs}$, defined as the volume to surface diameter of the particle, which for spherical particle of 1.75 mm diameter, as received, was calculated as 0.30 mm, for halves as 0.20 mm, and for quarters as 0.10 mm.

**Table 1.** Specifications of the reactor assembly.

| Description | Specification |
|---|---|
| Length of the reactor tube | 600 mm |
| O.D. of the reactor tube | 15.1 mm |
| I.D. of the reactor tube | 11.2 mm |
| Length of the thermowell | 550 mm |
| Thermowell external diameter | 4 mm |
| Thermowell internal diameter | 2 mm |
| Recommended operating temperature | 550°C |
| Maximum working pressure | 1.013 bar |

For each run 2.0 g of the catalyst was used. Calcination and reduction of the catalyst were done *in situ*. Reduction step was performed for all three catalyst forms; however, calcination was performed only for the spherical form. The calcination was conducted at 500 °C under air flow of 100 ml/min for 5 h, while reduction was done under 100 ml/min hydrogen flow at 450 °C for 16 h. The reactor wall temperatures were maintained at 380 and 430 °C, $H_2$/MCH ratios were 0 and 8.4 and molal space velocity was in the range of $3.09\times10^4$ to $2.46\times10^5$ s·g-cat/mol MCH. All experiments were performed under atmospheric pressure. MCH was obtained from Sigma-Aldrich with purity of 99.0 wt%. Hydrogen gas was taken from BOC with purity greater than 99.995 mol%. Reaction products were analyzed by GC-FID system containing non-polar capillary column (BP-5: 5% phenyl and 95% dimethylpolysiloxane).

## RESULTS AND DISCUSSION

### Catalytic Experiments

Fig. 2 shows the effect of the ratio of the reactor internal diameter to nominal catalyst particle size on the conversion of methylcyclohexane. The nominal particle size as defined earlier is the volume to surface diameter of the particle. It is shown that under all three ratios, conversion increases with an increase in $W/F_{A0}$. The conversion of MCH increases dramatically when the catalyst is halved. For example, the

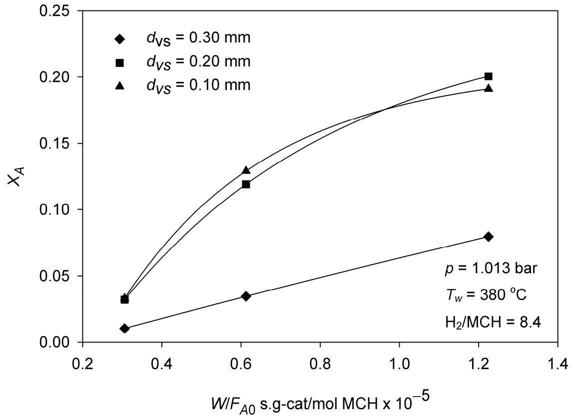

**Fig. 2.** Effect of particle size on methylcyclohexane conversion.

conversion increases more than two folds from 8.0% to 19.1% for the highest $W/F_{A0}$ at 380 °C wall temperature and 8.4 $H_2$ to MCH ratio. However, decreasing the catalyst particle from half ($d_{vs}$ = 0.20 mm) to quarter ($d_{vs}$ = 0.10 mm) gives virtually no difference. Overall methylcyclohexane was only fairly dehydrogenated at the wall temperature of 380 °C in the presence of hydrogen using $H_2$/MCH molar ratio of 8.4. The maximum conversion was only 20.1% even at the highest $W/F_{A0}$ ratio used which was $1.24 \times 10^5$ s.g-cat/mol MCH in the present case. An enhanced methylcyclohexane conversion with decrease in catalyst particle size may be explained on the basis of channeling phenomenon. With large particles, the bed voidage was too large especially near the wall of the reactor. This caused poor contact of gaseous MCH and the catalyst particles. A decrease in the particle size, however, improved the contact and hence the conversion. It is important to mention here that diffusion was not the reason because the catalyst was an egg-shell type. As further decrease in the size beyond $d_{vs}$ = 0.20 mm had virtually no beneficial effects; therefore, the remaining experiments were performed on the halved particles ($d_{vs}$ = 0.20 mm). This might be because voidage beyond this value was not appreciably influencing the flow patterns.

Fig. 3 compares the results with and without hydrogen in the feed. It is observed that methylcyclohexane conversion is a strong function of hydrogen addition and decreases strongly when hydrogen is in the feed. Hydrogen is a reaction product; therefore, the presence of hydrogen in feed was expected to decrease the dehydrogenation rates. Moreover, in the catalytic reaction, hydrogen may compete for the active sites and can provide product inhibition. Again at highest $W/F_{A0}$, conversion increases more than twice when there is no hydrogen in the feed. It was observed that the conversion could reach up to 21.4% and 49.0%, respectively, for the lowest and highest values of $W/F_{A0}$ used.

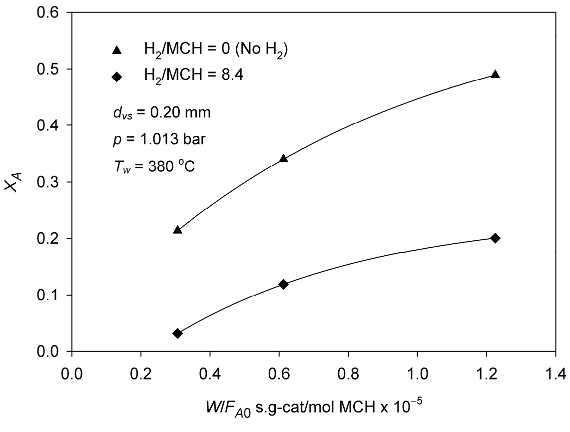

**Fig. 3.** Effect of hydrogen presence in the feed (feed composition) on methylcyclohexane.

Fig. 4 shows the effect of reactor wall temperature on MCH conversion without hydrogen in the feed. At the wall temperature of 430°C, substantial improvement in conversion is observed as expected. At that temperature, 97.5% methylcyclohexane was dehydrogenated at $2.46 \times 10^5$ s·g-cat/mol MCH. Under all conditions of temperatures, with and without hydrogen, the catalyst proved to be very selective towards toluene and no appreciable byproducts were observed.

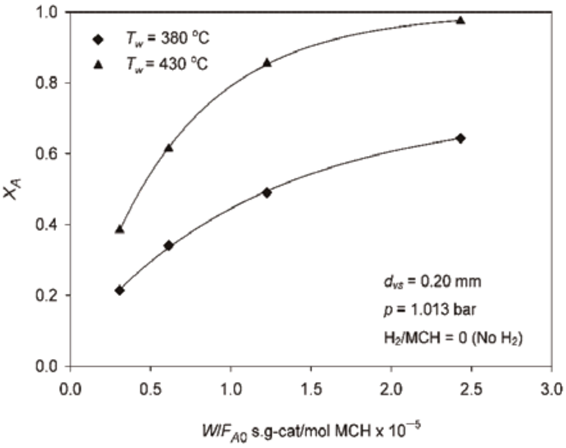

**Fig. 4.** Effect of reactor wall temperature on methylcyclohexane conversion.

## Kinetic Modeling

The experimental data obtained over 0.30 wt% $Pt/Al_2O_3$ catalyst was subjected to kinetic analysis. The fixed bed reactor was assumed to follow one dimensional plug flow reactor and the following expression was used to model the reaction kinetics.

$$\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)} \tag{3}$$

The rate of reaction, $(-r_A)$, is expressed in terms of the partial pressures of reacting species via the first order power law kinetics:

$$(-r_A) = k \cdot \left( p_A - \frac{p_B \cdot p_C^3}{K} \right) \tag{4}$$

where, $K$ is equilibrium constant for methylcyclohexane dehydrogenation and is given by [10]:

$$K = 3600 \cdot \exp\left(\frac{-217650}{R}\left(\frac{1}{T} - \frac{1}{650}\right)\right) \tag{5}$$

with $K$ in bar$^3$, $R$ in J·mol$^{-1}$·K$^{-1}$, and $T$ in K.

The rate constant $k$ is assumed to follow the Arrhenius temperature dependency and may be written as:

$$k = k_0 \cdot \exp\left(\frac{-E}{R \cdot T}\right) \tag{6}$$

Eq. 6 is reparameterized, as follows, in terms of $k_r$ ($k$ at the reference temperature, $T_r$), to reduce the correlation among the parameters and to converge the solution more rapidly.

$$k = k_r \cdot \exp\left(B \cdot \left(1 - \frac{T_r}{T}\right)\right) \tag{7}$$

where, $B$ is dimensionless activation energy and is given by:

$$B = \frac{E}{R \cdot T_r} \tag{8}$$

and $T_r$ is the reference temperature which is taken as 661.8 K.

The regression of the kinetic data was carried out using FORTRAN routine based on Marquardt algorithm; and sum of squares of the errors (objective function) was minimized.

Details of the above equations and the regression analysis may be found in Usman [7].

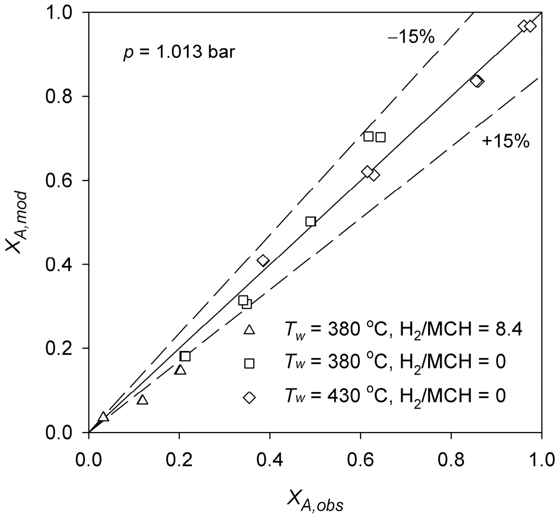

**Fig. 5.** Scatter diagram between observed conversion and model or calculated conversion.

Fig. 5 is the scatter diagram relating observed conversion and model conversion. Most of the data were observed to be fitted within ±15% error and showed an overall good fit to the first order reversible kinetics. Apparent activation energy was calculated as 100.6 kJ/mol and $k_r$ as 1.65 × 10$^{-5}$ mol·s$^{-1}$·g-cat$^{-1}$·Pa$^{-1}$.Touzani et al. [11], Van Trimpont et al. [12], Rimensberger [13] and Manser Sonderer [14] by studying the dehydrogenation reaction over Pt containing alumina catalysts also found values close to the above activation value.

## CONCLUSIONS

The dehydrogenation reaction was strongly affected by catalyst particle size, temperature and feed composition. MCH conversion reached 97.5% in the absence of hydrogen at 430 °C wall temperature and a space velocity of 2.46×10$^5$ s·g-cat/mol MCH. First order reversible kinetics was found appropriate to fit the experimental data. Apparent activation energy was 100.6 kJ/mol.

## NOMENCLATURE

| | |
|---|---|
| $B$ | dimensionless activation energy |
| $d_{vs}$ | volume to surface diameter, m |
| $F_{A0}$ | initial molar flowrate of methylcyclohexane (MCH), mol/s |
| $\Delta h^{\circ}_{rxn}$ | standard heat of reaction, J/mol |
| $k$ | rate or velocity constant, mol·s$^{-1}$·kg-cat$^{-1}$·Pa$^{-1}$ |
| $k_r$ | rate constant at reference temperature, mol·s$^{-1}$·kg-cat$^{-1}$·Pa$^{-1}$ |
| $k_0$ | frequency factor, mol·s$^{-1}$·kg-cat$^{-1}$·Pa$^{-1}$ |
| $K$ | dehydrogenation reaction equilibrium constant, Pa$^3$ |
| $p_A$ | partial pressure of methylcyclohexane, Pa |
| $p_B$ | partial pressure of toluene, Pa |
| $p_C$ | partial pressure of hydrogen, Pa |
| $(-r_A)$ | rate of the dehydrogenation reaction, mol·s$^{-1}$·kg-cat$^{-1}$ |
| $R$ | universal gas constant, m$^3$·Pa·K$^{-1}$·mol$^{-1}$ |
| $T$ | average temperature, K |
| $T_r$ | reference temperature, K |

| | |
|---|---|
| $W$ | weight of the catalyst, kg |
| $X_A$ | fractional conversion of methylcyclohexane to toluene |
| $X_{A,obs}$ | observed fractional conversion |
| $X_{A,mod}$ | model or calculated fractional conversion |

## ACKNOWLEDGMENT

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