

## MODELING OF METHYLCYCLOHEXANE TRANSFORMATION OVER A USHY ZEOLITE

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Key words: USHY zeolite, modeling, methylcyclohexane

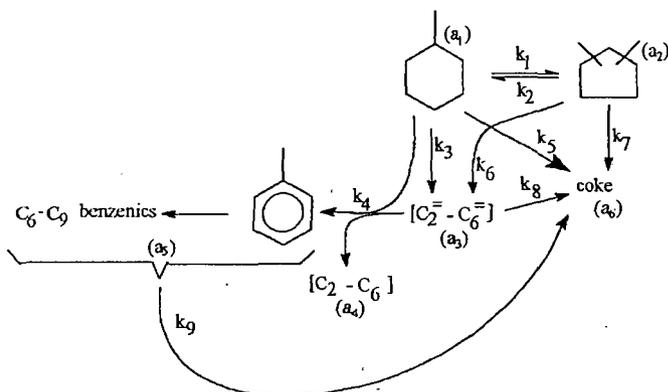
### ABSTRACT

A kinetic model with functions of deactivation by coke has been developed for the transformation of methylcyclohexane (isomerization, cracking, hydrogen transfer and coking) in a fixed bed reactor at 450°C over a USHY zeolite. A good fitting is obtained showing that the function of deactivation by coke depends on contact time.

### INTRODUCTION

Although naphthenes are important constituents of feedstocks and products of FCC (fluid catalytic cracking) little work has been reported in the literature [1,2]. This study concerns the transformation of methylcyclohexane over an USHY zeolite in a fixed bed reactor at 450°C.

From the effect of contact time the following reaction scheme was proposed to explain the formation of various products over the fresh catalyst.



Methylcyclohexane ( $a_1$ ) is isomerized into dimethylcyclopentanes ( $a_2$ ).  $C_2$ - $C_6$  alkenes ( $a_3$ ) are formed from double cracking of  $a_1$  and  $a_2$  followed by oligomerisation cracking steps. Methylcyclohexane is also transformed into toluene through hydrogen transfer towards  $a_3$  with formation of  $C_7$ - $C_9$  alkanes ( $a_4$ ), three moles of  $a_3$  being transformed per mole of  $a_1$ . Toluene undergoes disproportionation with formation of benzene, xylenes and trimethylbenzenes. Coke results mainly from  $C_3$  products (which are not observed) of the simple cracking of  $a_1$  and  $a_2$  but is also formed from  $a_3$  and from aromatics ( $a_5$ ).

A kinetic model with deactivation functions was developed allowing the complete description of the transformation of methylcyclohexane.

### MATERIALS AND METHODS

The USHY zeolite ( $Na_{3.4}H_{3.4.5}Al_{34.9}Si_{157.1}O_{844}$ , 17.8 extra framework aluminium) resulted from calcination under air flow, at 500°C for 12 h of an ultrastable  $NH_4$  zeolite (CBV 500 from PQ). Methylcyclohexane transformation was carried out in a fixed bed reactor at 450°C  $p/V_2 = 0.9$  bar,  $p_{methylcyclohexane} = 0.1$  bar at various contact times. Reaction products were analyzed on-line by gas chromatography with a 50 m fused silica capillary column Plot  $Al_2O_3/KCl$ .

The mathematical model has been previously described [3]. From the reaction scheme, assuming elementary steps, a plug flow behaviour uniform porosity and quasi-steady-state, the following equations may be written:

$$\frac{\partial a_1}{\partial Z} = \frac{P}{WHSV \cdot R \cdot T \cdot \sum_{i=1}^5 a_i} \cdot [k_2 \cdot a_2 \cdot \phi_1 - (k_1 \cdot \phi_1 + k_3 \cdot \phi_3 + k_4 \cdot a_3 \cdot \phi_3 + k_5 \cdot \phi_{\text{cokc}}) \cdot a_1] \quad (1)$$

$$\frac{\partial a_2}{\partial Z} = \frac{P}{WHSV \cdot R \cdot T \cdot \sum_{i=1}^5 a_i} \cdot [k_1 \cdot a_1 \cdot \phi_2 - (k_6 \cdot \phi_3 + k_2 \cdot \phi_1 + k_7 \cdot \phi_{\text{cokc}}) \cdot a_2] \quad (2)$$

$$\frac{\partial a_3}{\partial Z} = \frac{P}{WHSV \cdot R \cdot T \cdot \sum_{i=1}^5 a_i} \cdot [(v_1 \cdot k_3 \cdot a_1 + v_2 \cdot k_4 \cdot a_2) \cdot \phi_3 - (3 \cdot k_4 \cdot a_1 \cdot \phi_3 + k_5 \cdot \phi_{\text{cokc}}) \cdot a_3] \quad (3)$$

$$\frac{\partial a_4}{\partial Z} = \frac{P}{WHSV \cdot R \cdot T \cdot \sum_{i=1}^5 a_i} \cdot (3 \cdot k_4 \cdot a_1 \cdot a_3 \cdot \phi_4) \quad (4)$$

$$\frac{\partial a_5}{\partial Z} = \frac{P}{WHSV \cdot R \cdot T \cdot \sum_{i=1}^5 a_i} \cdot [(k_4 \cdot a_1 \cdot a_3 \cdot \phi_4) - k_5 \cdot a_3 \cdot \phi_{\text{cokc}}] \quad (5)$$

$$\frac{\partial a_6}{\partial Z} = \frac{P}{WHSV \cdot R \cdot T \cdot \sum_{i=1}^5 a_i} \cdot (v_3 \cdot k_3 \cdot a_1 + v_4 \cdot k_7 \cdot a_2 + v_5 \cdot k_8 \cdot a_3 + v_6 \cdot k_9 \cdot a_4) \cdot \phi_{\text{cokc}} \quad (6)$$

$$\frac{\partial a_7}{\partial t} = \frac{P}{R \cdot T \cdot \sum_{i=1}^5 a_i} \cdot (v_3 \cdot k_3 \cdot a_1 + v_4 \cdot k_7 \cdot a_2 + v_5 \cdot k_8 \cdot a_3 + v_6 \cdot k_9 \cdot a_4) \cdot \phi_{\text{cokc}} \quad (7)$$

Where,  $a_i$  is the concentration of the  $a_i$  species [mols of lump  $i$  / g gas],  $a_7 = C_c$  is the coke content on catalyst [wt%],  $k_i$  is the kinetic constant for the reaction  $i$ ,  $t$  is the time-on-stream,  $Z$  is the dimensionless axial position,  $v_1 = v_2$  is the ratio between the molecular weight of methylcyclohexane and olefins,  $v_3 = v_4$  is the molecular weight of methylcyclohexane,  $v_5$  is the molecular weight of olefins,  $v_6$  is the molecular weight of aromatics,  $\phi_i$  is the deactivation function for reactions leading to the correspondent  $a_i$  specie and  $\phi_{\text{cokc}}$  is the deactivation function for reactions leading to coke.

The mathematical solution was performed by finite difference discretization of the reactor with respect to the axial position. For a given set of kinetic constants and deactivation parameters, the system solution was obtained by backward finite differences formula with variable step, implemented in the DASSL code [4,5]. The initial condition is that the reactor is full of nitrogen. Although numerical convergence for a relative tolerance of 10<sup>-7</sup> was obtained only for 120 discretization elements, satisfactory results are obtained for 10 discretization elements.

## RESULTS AND DISCUSSION

### Deactivation Functions

The deactivation functions may be related to the true deactivating agent, i.e., coke itself [6,7]. One parameter functions (eq. 8) which provide results very similar to those obtained with multiparameter functions [8] were chosen for all the reaction steps except for coke formation. However as coke may alter the product distribution, the deactivation parameter ( $\alpha$ ) should depend on the step.

It is generally found that at short time-on-stream, which corresponds to the formation of the first coke molecules, coke formation itself is not deactivated. Deactivation becomes very pronounced when the coke molecules attain a size comparable to that of zeolite cages because the access of the coke-maker molecules becomes difficult. In order to consider this particular mode of deactivation the deactivation function given in equation 9 was used for all reactions leading to coke.

The limit coke content ( $C_{\text{lim}}$ ) above which the coke affects its formation was obtained from the change in coke content as a function of time-on-stream. Many values were considered for the  $A$  constant, a value of 180 being finally found to be appropriate.

$$\phi_i = \exp(-\alpha_i \cdot C_c) \quad (8)$$

$$\phi_{\text{cokc}} = \frac{1}{\exp[A \cdot (C_c - C_{\text{lim}})] + 1} \quad (9)$$

### Parameter Estimation

Different approaches were tested to improve the convergence of a maximum likelihood method [9]. Sequential parameter estimation, centering [10], model reformulation, using only either initial or iso-coke data and also trial and error change of initial values. Experimental error estimation was made with five replicates for one time-on-stream of 30 min and a WHSV (weight hourly space velocity) of 62.

Firstly, relations between the deactivation parameters ( $\alpha$ ) were established. To achieve this goal the residual activities as a function of coke on catalyst should be determined for all the reaction steps, the initial activities (at zero coke content) being estimated by extrapolation of the curves giving the product yield vs. time-on-stream. The following relations between parameters were obtained.

$$\alpha_1 = \alpha_2 = \alpha \quad (10)$$

$$\alpha_3 = 1.6 \cdot \alpha \quad (11)$$

$$\alpha_4 = \alpha_5 = 1.8 \cdot \alpha \quad (12)$$

Good fitting is obtained for each contact time but the value of  $\alpha$  seems to depend on contact time, which indicates that the location of coke, hence its deactivating effect changes with this parameter ( $\alpha$ ). Indeed when coke molecules are located near the pore mouth, their blockage effect is more significant than when they are homogeneously distributed in the crystallite [11].

The values of  $\alpha$  which give the best results increase with contact time from 3 (WHSV = 500) to 12 (WHSV = 62), i.e. the longer the contact time, the less homogeneous the coke distribution in the zeolite crystallites. With these values of  $\alpha$  a good agreement is found between experimental results and model curves (figs. 1 to 3). The objective likelihood function presented a relative reduction of 25%.

The kinetic constant values are presented in Table 1. For isomerization of methylcyclohexane the  $k_1/k_2$  ratio is determined from thermodynamic data [12].

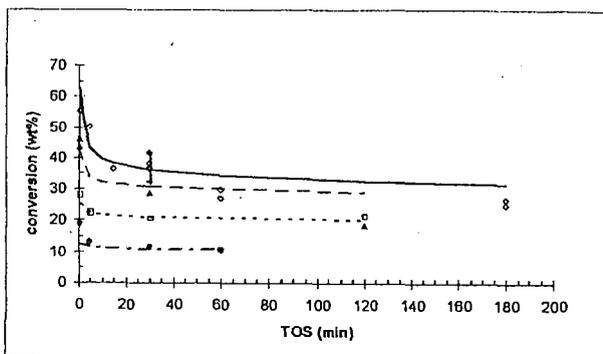


Figure 1: Conversion of methylcyclohexane versus time-on-stream (TOS). Calculated curves and experimental data for 4 different contact times.

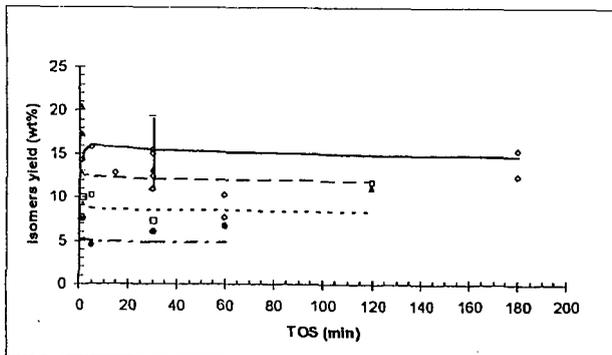


Figure 2: Isomers yield versus time-on-stream (TOS). Calculated curves and experimental data for 4 different contact times.

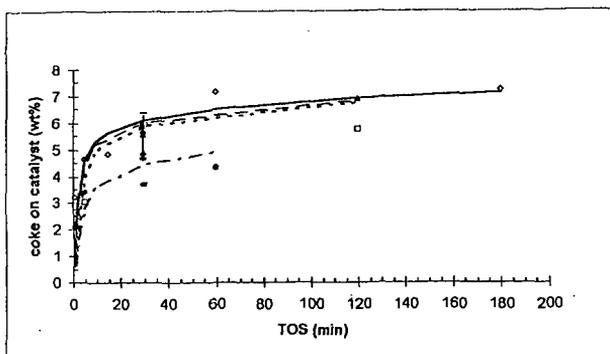


Figure 3: Coke on catalyst versus time-on-stream (TOS). Calculated curves and experimental data for 4 different contact times.

Table 1 : Kinetic constants

kinetic constant	value	kinetic constant	value
$k_1$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$8.5 \times 10^4$	$k_6$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$1.7 \times 10^5$
$k_2$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$0.417 \cdot k_1$	$k_7$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$3.5 \times 10^4$
$k_3$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$7.0 \times 10^4$	$k_8$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$8.5 \times 10^3$
$k_4$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·(g/mol)·h <sup>-1</sup> ]	$3.3 \times 10^9$	$k_9$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$5.7 \times 10^3$
$k_5$ [(g cat/cm <sup>3</sup> ) <sup>-1</sup> ·h <sup>-1</sup> ]	$2.0 \times 10^3$		

## CONCLUSIONS

The reaction scheme of methylcyclohexane transformation over a USHY zeolite was established. A kinetic model was developed to represent the change versus time-on-stream of the product yields. A kinetic model was obtained showing that the function of deactivation by coke depends on contact time and then on the coke location inside the zeolite.

## ACKNOWLEDGEMENTS

The support of CAPES foundation (Brazilian government), FCC S.A. and UMR CNRS 6503 is gratefully acknowledged.

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