Toward a Reliable Computational Description of Hydrocarbon Activation in Zeolites: A Study of Cracking, Dehydrogenation, and H/D Exchange of Alkanes in H-ZSM-5

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Introduction: During the past decade, quantum-chemical calculations have been used to model hydrocarbon reactions in zeolite acid catalysts. In the interest of computational feasibility, the zeolite has often been represented by a very small cluster model, at times including only one tetrahedrally-coordinated atom (a 1T cluster). The results of such calculations have given important qualitative insights such as possible reaction pathways and transition state geometries, but the calculated activation energies for hydrocarbon reactions have usually been 50 percent or more higher than experimental values. In our recent work we developed a methodology of quantum-chemical techniques and corrections that allowed us to calculate a quantitatively accurate activation energy for protolytic cracking of ethane in H-ZSM-5 [1]. In order to test the limits of our computational method, we have carried out a study of protolytic cracking, dehydrogenation, and H/D exchange of the n-alkanes ethane, propane, and butane using a cluster model of H-ZSM-5. Our goal is to study the dependence of the activation energy on the alkane chain length in these reactions and to determine whether this method can produce results in quantitative agreement with available experimental results [2-5].

Theoretical Methods: We obtained the optimized geometries and zero-point energies of structures on each reaction pathway using the HF/6-31G(d) method and the B3LYP/6-31G(d) level of density functional theory. Our transition state structures have only one imaginary vibrational frequency, corresponding to the reaction coordinate. Our cluster model for the zeolite framework, denoted 5T, has five tetrahedrally-coordinated atoms and is terminated by H atoms at its periphery. This cluster model is much larger than the 1T model used in much previous work [6] and is better able to represent interactions of an adsorbed hydrocarbon molecule with framework oxygen atoms near the Bronsted site in the zeolite. To determine the activation barriers for each reaction, we calculated corrections for (i) scaled zero-point energies and thermal corrections for the experimental reaction temperature of 773 K; (ii) an extended basis set, calculated at the B3LYP/6-31+G(3df,2p) level; and (iii) the long-range electrostatic effects of the zeolite framework. The electrostatic correction was determined by performing a partial optimization of each transition state in a larger 18T zeolite cluster model and then embedding the resulting structure into a much larger 64T cluster model, constructed from the experimental geometry of H-ZSM-5.
RESULTS AND DISCUSSION:

As an example of our results, a schematic potential energy surface for the complete reaction pathway for catalytic cracking of propane is shown in Fig. 1. Starting from an adsorbed complex (20H"-C3H8), the acidic proton attacks a terminal C-H bond. Via an ionic transition state (ZO--C3H9+) this forms C3 and a surface-bound ethoxy species (ZOCZHJ. In order to close the catalytic cycle, a proton is abstracted from the ethoxy species by a nearby framework oxygen atom. This proceeds through another transition state (ZOH--C2H4) to form a new Bronsted acid site with an adsorbed ethene molecule (ZOH"-CZH4). When the energy corrections described above are used to calculate the true energy barrier for propane cracking, we obtain a final value of 43 kcal/mol, in good agreement with the experimental value of 47 ± 3 kcal/mol [3]. Similar results for dehydrogenation and H/D exchange reactions will be presented and discussed.

Fig. 1. Schematic potential energy surface for propane cracking. Energies in parentheses include zero-point corrections.

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ABSTRACT

The objectives of this presentation are two-fold: first, to demonstrate the connection between the attainable coefficients and transition to turbulent flow by using the transition-based corresponding states method to generalize results obtained with smooth tubes and enhanced tubes, and second, to provide guidelines on the calculation of heat transfer coefficients from pressure-drop data and vice versa by using the transition concept or the frictional law of corresponding states.

INTRODUCTION

It is well established that the onset of transition to turbulent flow manifests itself through a sharp rise in pressure, whether by the pressure gradient or the static pressure in the flowing fluid. Consistent with the connection between friction and heat transfer, the results already presented in Part I show that the Nusselt number increases sharply almost at the onset of the transition to turbulence. Accordingly, there is remarkable consistency in the values of the transition Reynolds number determined from friction factor and Nusselt number results.

In the absence of transition to turbulent flow, laminar flow trends prevail for both friction factor and Nusselt number with increasing Reynolds number, i.e., \( f \propto Re^1 \) and \( \text{Nu} \propto Re^{1/2} \). Thus, transition is important because it gives rise to \( f \) or \( \text{Nu} \) dependence on \( Re \) that is vastly different from that for laminar flow. Consequently, values of \( f \) or \( \text{Nu} \) differ markedly between laminar and turbulent flow for equal Reynolds number.

The origin of the corresponding states concept was the analysis of friction factor results obtained in circular and noncircular smooth passages (Obot, 1988). The conclusion was that differences in friction factor were due to the inseparably connected effects of transition to turbulent flow and the length scale used to reduce the data to nondimensional form. Allowing for the differences in values of the critical friction factor and Reynolds number, the friction factor results for circular and noncircular passages were completely generalized. Attempts to extend the analysis to heat transfer were frustrated by lack of verifiable laminar flow heat transfer data. Hence, an extensive experimental study was initiated to provide the needed data for a range of tube geometry and working fluids (Esen, 1992; Das, 1993).

In this paper, the results presented in Part I are used to demonstrate the connection between the transfer coefficients and the transition process by using the corresponding states concept. Guidelines on the use of the correlations developed herein to calculate heat transfer coefficients or pressure drop for smooth or enhanced tubes are provided and discussed.

ANALYSIS

For the convenience of the reader, the applicable equations are briefly outlined here. Additional information is provided in Obot et al. (1994). With the corresponding states method, reference critical values for the transition Reynolds number, friction factor and Nusselt number are used to scale arbitrary sets of data according to the following relationships:

\[
Re_m = \left( \frac{Re_{c,r}}{Re_{c,a}} \right) Re_a \tag{1}
\]

\[
f_m = \left( \frac{f_{c,r}}{f_{c,a}} \right) f_a \tag{2}
\]

\[
\text{Nu}_m = \left( \frac{\text{Nu}_{c,r}}{\text{Nu}_{c,a}} \right) \text{Nu}_a, \tag{3}
\]

where \( Re_{c,r}, f_{c,r}, \) and \( \text{Nu}_{c,r} \) correspond to the values of the transition Reynolds number, friction factor, and Nusselt number at the onset of turbulence for a reference data set, i.e., for the smooth-tube in this study), and \( Re_{c,a}, f_{c,a}, \) and \( \text{Nu}_{c,a} \) are the corresponding transition parameters for any arbitrary set of results.

In the laminar regime, the well-known relationship between the friction factor and Reynolds number is
\[ f \times Re = C_f, \quad (4) \]

where \( C_f \) is a constant for each tube. Similarly, for heat transfer in laminar flow, the expression for the Nusselt number is

\[ Nu/Re^{1/2} = C_h, \quad (5) \]

where \( C_h \) is also a constant for each tube. Allowing for the Prandtl number dependence by using the 0.4 power dependence, Eq. (5) becomes

\[ Nu(Re^{1/2} Pr^{0.4}) = C_h. \quad (6) \]

Equations (4) and (6) for \( C_f \) and \( C_h \) are combined to give

\[ C_h/C_f = Nu(Re^{3/2} Pr^{0.4}). \quad (7) \]

The reduced form of Eq. (7), which accounts for variations in the transition parameters, is

\[ C_{h,m}/C_{f,m} = Nu_m/(Re_m^{3/2} f_m Pr^{0.4}). \quad (8) \]

Alternatively, the results for all Prandtl numbers can be generalized without incorporating Prandtl number dependence. This is accomplished simply by selecting a common reference for all results and the applicable equation takes the form

\[ C_{h,m}/C_{f,m} = Nu_m/(Re_m^{3/2} f_m). \quad (9) \]

Equations (8) and (9) are general statements of the friction-heat transfer analogy. Although the formulation is based on laminar flow observations, there is no reason that these relationships should not hold for turbulent flow.

**RESULTS AND DISCUSSION**

It is emphasized that for the presentation that follows, only the final correlations are considered and shown graphically. The general trends for the individual variables (\( C_f \), \( C_{f,m} \), \( C_h \), \( C_{h,m} \), and \( C_{h,m} \)) were presented in graphical form and discussed in several publications (Obot et al., 1994; Esen, 1992; Das, 1993); hence, they are not shown or discussed in this paper.

To begin presentation and discussion, attention is directed to Figs. 1-3. In Fig. 1, the fit of the laminar flow results to the correlation given in Part I is illustrated graphically; the results for the smooth tube (0.7 \( \leq Pr \leq 125.3 \)) and enhanced tube (0.7 \( \leq Pr \leq 24.8 \)) are included in the figure. Figure 2 is an alternative representation of the same laminar flow results; Eqs. (1)-(3) are used to account for the differences in the transition parameters. Figure 3 was prepared by using the transition parameters presented in Table 2 of Part I and shows the relationship between \( Nuc \), \( Re_c \), and \( f_c \).
It is evident that although the regression coefficient of 0.008 provides close approximation of the results in Figs. 1 and 2, the latter is characterized by less spread of the data. Accordingly, about 90% of the data points are predicted with errors that are mostly under 30% in Fig. 1; the error band is under 20% for 95% of the data in Fig. 2. The indication is that there is little influence of the transition process on laminar flow correlation. As might be expected because the $Re$ and $f$ values at the onset of transition must satisfy the laminar flow flow solution, the same regression constant provides satisfactory representation of the transition parameters ($Nu_t$, $f_c$, and $Re_c$) in Fig. 3.

If the subscripts are eliminated, the recommended correlation for calculation of laminar flow transfer coefficients, including the critical values at the onset of transition to turbulent flow, is

$$\overline{C_h}/C_f = Nu(Re^{3/2}fPr^{0.4}) = 0.008. \tag{10}$$

Equation (10) provides satisfactory estimates of the transfer coefficients, within the accuracy of experimental errors.

The practical significance of the trends in the laminar flow correlation relates to the calculation of transitional/turbulent-flow Nusselt numbers, inasmuch as experimental determination of all three transition parameters ($f_c$, $Nu_t$, and $Re_c$) is not necessary. For instance, use of laminar flow pressure-drop results, i.e., a plot of $C_f (= f x Re)$ versus $Re$, gives $C_{fe} (= f_c x Re_c)$, and $Re_c; f_c$ is readily obtained by using the known $Re_e$. The remaining critical parameter, $Nu_t$, is calculated from Eq. (10). With $Re_e$, $f_c$, and $Nu_t$ established, the friction factor/Nusselt number calculations proceed as outlined subsequently.

For the transition and turbulent regimes, it was noted in Part I that the $C_{h}/C_f$ versus $Re$ data followed the same trend for both flow types. Also, it was mentioned that correlation of the $Nu$ results in terms of $f, Re$, and $Pr$ was not possible due to the residual effects of roughness geometry. These observations can be inferred from the plot of $C_{h}/C_f$ versus $Re$ presented in Fig. 4. This figure was prepared by using results for the smooth tube and enhanced tubes, a total of 1023 data points.

Figures 5 and 6 are alternative representations of the results in Fig. 4; the data reduction formats correspond respectively to Eqs. (8) and (9). For the sake of completeness, the laminar flow results are included in Figs. 5 and 6. In Fig. 5 and for each $Pr$ value, the values for the reference transition parameters are those for the smooth tube with the particular Prandtl number. Values of the transition parameters were presented in Table 2 of Part I. For Fig. 6, the values for the reference transition parameters were 6.0, 0.009, and 2100 for $Nu_t$, $f_c$, and $Re_c$ respectively. The results were obtained with the smooth tube and air as the working fluid. Note that in terms of $C_{h,m}$ and $C_{f,m}$, the corresponding laminar flow correlation is $C_{h,m}/C_{f,m} = 0.0068$, with no $Pr$ dependence.

The implication of the trends in Fig. 5 or 6 is that, in terms of the expended power, laminar flow affords the best heat transfer performance relative to transitional and turbulent flow. This observation is of practical significance.
as it sheds light on the potential benefit of microscale heat and mass transfer. The unique feature of microheat exchangers and microreactors is the existence of mostly laminar flow; this is a primary reason for the interests in these devices.

For $Re_m \geq 2100$, the results in Fig. 5 are closely approximated by

$$\frac{C_{h,m}}{C_{f,m}} = \frac{Nu_m}{(Re_m/2f_m Pr^{0.4})} = 0.21 Re_m^{-0.45}. \quad (11)$$

With a common reference for all results (Fig. 6) that does not include a Prandtl number dependence, the correlation for $Re_m \geq 2100$ is

$$\frac{C_{h,m}}{C_{f,m}} = \frac{Nu_m}{(Re_m/2f_m)} = 0.18 Re_m^{-0.45}. \quad (12)$$

The scatter plots for Eqs. (11) and (12) are presented in Figs. 7 and 8, respectively; the appropriately calculated values for laminar flow are also included in the plots. It is evident from comparisons between Figs. 5 and 6, or between Figs. 7 and 8, that the use of a common reference gives slightly better collapse of the results. The remarkable collapse of unrelated $\frac{C_{h,m}}{C_{f,m}}$ or $C_{h,m}/C_{f,m}$ versus $Re_m$ data for $Re_m \geq 2100$, with deviations that are much better than can be expected from this type of experiments, provides verification of the role of transition. It is apparent that the results for both transitional and turbulent flow regimes are effectively correlated with a single equation, with no additional parameters to account for the enhanced-tube geometric details.

Since Eq. (11) or (12) is valid for smooth tubes, its general form can be compared to conventional correlations, at least insofar as the dependence of $Nu_m$ (or $Nu$) on $Re_m$ (or $Re$) is concerned. For instance, in terms of the reduced variables, the combination of the Blasius equation ($f_m = 0.079Re_m^{-0.25}$) and the Dittus-Boelter equation ($Nu_m = 0.023Re_m^{0.8}Pr^{0.4}$) gives $Nu_m/f_m = 0.29Re_m^{1.05}Pr^{0.4}$; the exponent on $Re_m$ compares favorably with $Nu_m/f_m = 0.21Re_m^{1.05}Pr^{0.4}$ from Eq. (11).

The comparison of Eq. (11) with the well-known Petukhov-Popov (1963) correlation was made quantitatively for the $2100 < Re_m < 10^5$ covered in this study by replacing $Nu$, $f$, and $Re$ in the original correlation by $Nu_m$, $f_m$, and $Re_m$, respectively. Relative to the Petukhov-Popov correlation, Eq. (11) gives consistently lower values.Expressed as percentages, the deviations are generally within 1 to 20%, with an average value of $\pm 1\%$. The primary reason for these deviations is that the physical properties (except for $\mu_b$ and $\mu_w$) in the original Petukhov-Popov correlation are based on the film temperature, in contrast to the use of bulk properties (except $\rho_v$ for friction factor) in this study. Nevertheless, this degree of concurrence demonstrates that heat-transfer coefficients for enhanced tubes can be calculated from smooth-tube correlations using the procedures outlined below in this paper.

Finally, it is worthy of note that Eq. (11) reduces to the well-known Reynolds analogy for $Pr = 0.7$. It is easily established that in terms of the reduced Stanton number $(St_m)$, reduced friction factor $(f_m)$, and the Prandtl number $(Pr)$, Eq. (11) is approximated by

$$St_mPr^{0.6} = 0.4 f_m. \quad (13)$$

The validity range for this equation is $2100 \leq Re_m \leq 10^5$. It is evident that $St_m \approx (1/2)f_m$ for $Pr = 0.7$, in line with the Reynolds analogy. However, unlike the familiar Reynolds analogy, Eq. (13) holds for both smooth and enhanced tubes at the same reduced conditions. The outcome of the analysis supports the $1/2$ power dependence of $Nu$ on $Re$ in laminar flow. For $Re_m \geq 2100$, the calculated values from Eq. (13) are generally within 30% of the experimental values. So a general form of the friction and heat-transfer analogy that is consistent with the Reynolds analogy is developed for smooth and enhanced tubes.
Calculation of Nusselt Number or Friction Factor

As noted previously, one objective of this study was to develop a general predictive method for the heat transfer and pressure drop of smooth and enhanced tubes. The correlations presented herein afford calculations of Nusselt number from friction factor data for a specified Reynolds number range, and vice versa. With the transition parameters for \( Pr = 0.7 \) \( (f_{c,r} = 0.009, Nu_{c,r} = 6.0, \) and \( Re_{c,r} = 2100) \) as the reference, the calculation procedures are outlined as follows:

1. In laminar flow and for \( 0.7 \leq Pr \leq 125, \) the unscaled correlation (in terms of \( Nu, f, \) and \( Re \)) is the same as that at reduced conditions (in terms of \( Num, f_m, \) and \( Rem \)). For a given \( Pr, Nu \) is calculated from \( Re \) and \( f \), or \( f \), and hence the pressure drop is computed from \( Nu \) and \( Re \).

2. To calculate transitional- and turbulent-flow Nusselt numbers from friction factor-Reynolds number data, the steps are (a) determine the transition Reynolds number \( (Re_{c,a}) \) from the \( C_f \) versus \( Re \) plot using arbitrary data set; (b) compute \( f_{c,a} \) from \( f_{c,a} = C_f/Re_{c,a} \) and the transition Nusselt number \( (Nu_{c,a}) \) from \( Nu_{c,a} = 0.008Re_{c,a}^{3/2}f_{c,a}Pr^{0.4} \); (c) \( Rem \) and \( f_m \) are computed from Eqs. (1) and (2), respectively; and (d) \( Num \) and \( Nu_m \) are calculated from Eqs. (12) and (3), respectively.

3. The calculation of transitional- and turbulent-flow pressure drop from heat-transfer data from arbitrary data is carried out in a similar manner: (a) \( Re_{c,a} \) is obtained from a plot of \( C_h \) versus \( Re \); (b) \( Nu_{c,a} \) is computed from \( Nu_{c,a} = C_h/Re_{c,a} \) where \( C_h/C_f = 0.008 \); (c) \( Rem \) and \( f_m \) are computed from Eqs. (1) and (3), respectively; and (d) \( f_m \) and the required friction factor \( f_a \) from Eqs. (12) and (2), respectively.

It is evident from the above presentation that determination of the transition parameters is the key to the use of the transitional- and turbulent-flow correlations. From a practical standpoint, the calculation of heat transfer coefficients by using pressure drop data is preferred for several reasons. First, it involves determination of the transition values for the Reynolds number and friction factor, and these can be obtained with errors that are smaller than the uncertainties in measured heat transfer coefficients. Second, pressure-drop measurements are less time-consuming and are inexpensive. Third, there are straightforward and easily implemented methods for determination of the transition parameters from differential pressure measurements (Obob et al., 1991). In this regard, it is worth noting that use of the pressure-drop ratio discussed in Part I gives \( Re_c \) and \( f_c \) values with a 10% error band.

For circular smooth tubes, values of \( Re_c \) and \( f_c \) can differ from those used in this paper as the reference (Obot et al., 1994). Similarly, noncircular smooth passages are usually characterized by \( Re_c \) and \( f_c \) values that are not the same as those for circular smooth tubes when the experimental data are reduced using the hydraulic diameter or an arbitrarily-defined length scale (Obot, 1988). Under these conditions, Eqs. (1)-(3) must be used to calculate the reduced parameters needed for Eq. (11) or (12).

CONCLUSIONS

The frictional law of corresponding states has been validated from experimental results obtained for the \( 0.7 \leq Pr \leq 125.3 \) range. In laminar flow, the characteristic feature is the existence of stable flow for all Reynolds numbers. Accordingly, the results for smooth and enhanced tubes are completely generalized in terms of \( f, Nu, Pr, \) and \( Re \), and no corrections are needed to account for the effect of enhanced-tube geometric details or transition to turbulence. Judging from the results of the analysis, it appears that the laminar flow correlation is of general validity.

In terms of \( Pr \) and the reduced variables \( (f_m, Nu_m, \) and \( Rem) \) the transitional- and turbulent-flow results are adequately represented by a single equation, and no additional parameters required to account for the enhanced-tube geometric details. Alternatively, with the specified set of transition parameters \( (f_c, Nu_c, \) and \( Re_c) \) as the common reference for all results, a superior correlation in terms of \( f_m, Nu_m, \) and \( Rem \) is obtained with no Prandtl number dependence.

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**NOMENCLATURE**

$C_f$ friction parameter, $f x Re$

$C_h$ heat transfer parameter, $Nu/Re^{1/2}$

$\overline{C_h}$ heat transfer parameter, $Nu/Re^{1/2} Pr^{0.4}$

$f$ Fanning friction factor

$Nu$ Nusselt number

$Pr$ Prandtl number

$Re$ Reynolds number

$\mu_b$ fluid viscosity based on bulk temperature

$\mu_w$ fluid viscosity at $T_w$

$\rho_w$ fluid density evaluated at $T_w$

**Additional Subscripts**

$a$ arbitrary condition

c value at onset of transition

c, $a$ transition parameters for arbitrary condition

c, $r$ transition parameters for reference condition

$m$ value at reduced condition