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# The turnover frequency of methylcyclohexane dehydrogenation to toluene on a Pt reforming catalyst

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## Abstract

The dehydrogenation of methylcyclohexane to toluene is representative of one of the major types of reactions occurring in the catalytic reforming of petroleum naphtha fractions. An investigation of the kinetics of the reaction on a platinum reforming catalyst in the temperature range of 588–645 K was reported by the writer and coworkers in 1960. Included in that paper was a value of the reaction rate per unit surface area of platinum at 588 K, along with a rate expression permitting one to obtain such information over a range of reaction conditions. The determination of this intrinsic measure of the dehydrogenation activity of the 1 nm clusters of platinum in the catalyst was made possible by the work of Spenadel and Boudart on the development of a hydrogen chemisorption method for the evaluation of the platinum surface area. In the present paper, the writer reports the dehydrogenation activity of the platinum clusters in the form of a turnover frequency, a measure of catalytic activity advocated by Boudart analogous to that used by workers in enzyme catalysis. The writer then extrapolates the rate equation in the 1960 paper of Sinfelt and coworkers to determine a turnover frequency at a substantially higher temperature characteristic of a catalytic reforming operation, and compares this with a value at that temperature determined directly by experiment. Finally, the turnover frequency for methylcyclohexane is compared with that for its homolog cyclohexane. © 2000 Published by Elsevier Science B.V.

*Keywords:* Methylcyclohexane; Toluene; Catalytic reforming

## 1. Introduction

It is a special pleasure to be a contributor to this issue of the Journal of Molecular Catalysis honoring Michel Boudart. When I first met Michel late in 1954, he had just begun teaching at Princeton University and I was beginning my long association with the Exxon Research and Engineering Company (then known as the Standard Oil Development Company). Over many years that have elapsed since that time, we have had a continuing dialogue about various aspects of kinetics and catalysis. The topic of my short paper for this occasion is one in which Michel looms large in the background.

The dehydrogenation of methylcyclohexane to toluene (Fig. 1) is an example of a major type of reaction occurring in the catalytic reforming process for the production of high octane number components for gasoline [1–3]. The feasibility of conducting the reaction on platinum catalysts was first recognized by Zelinskii in 1911–1912 in his pioneering investigations on the dehydrogenation of cyclohexane and its homologs to aromatic hydrocarbons [4,5].

Observations that the reaction also occurred over certain transition metal oxides, notably molybdena and chromia dispersed on alumina, led to the exploitation of these oxide catalysts in the first commercial applications of catalytic reforming in the petroleum industry,

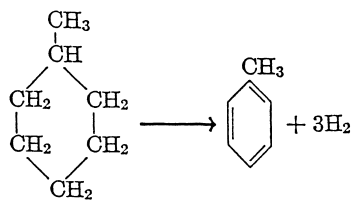


Fig. 1. The dehydrogenation of methylcyclohexane to toluene.

beginning in 1940 [6]. Eventually, a platinum catalyst was introduced in a commercial catalytic reforming unit in 1949 [7]. The initial reluctance to use the precious metal in a reforming catalyst was overcome by the recognition that its catalytic properties were clearly superior to those of the oxides for the process.

Catalysts containing very small amounts of platinum dispersed throughout the pores of high surface area aluminas were developed by a number of petroleum companies in the 1950s. The platinum contents of the catalysts were typically in the range of 0.3–0.6 wt.%. The surface of the alumina support commonly contained chlorine in an amount about equal to the weight fraction of platinum present, as a consequence of the use of chloroplatinic acid in the preparation of the catalyst. Additional chlorine could also be introduced, either before or after the catalyst was charged to a reforming unit.

The acidic properties of the alumina support depend on the amount of chlorine present. This is not important for the dehydrogenation activity of the catalyst, since only the platinum metal sites are needed for dehydrogenation reactions such as the conversion of methylcyclohexane to toluene. However, it is important for other reactions occurring in the catalytic reforming of the complex hydrocarbon mixtures characteristic of petroleum naphtha fractions. Such reactions include the conversion of alkylcyclopentanes and open-chain alkanes to aromatic hydrocarbons and the isomerization and hydrocracking reactions of alkanes. The bifunctional action of the catalyst, in which both the metal and acidic sites are involved in polystep reaction sequences, is important in all of these latter reactions [2,3,8].

Since we are concerned only with catalysis by platinum metal sites in methylcyclohexane dehydrogenation, we restrict our attention to the platinum component of the catalyst for the remainder of the paper. In the 1950s, it appeared very likely that the

platinum in a freshly prepared reforming catalyst was present in a highly dispersed state, since the platinum was not detectable in an X-ray diffraction pattern. However, there was no quantitative information available on the fraction of the platinum atoms that were present as surface atoms. To address this problem, Michel Boudart, in collaboration with Larry Spenadel, decided to measure the chemisorption of hydrogen on the platinum component of the catalyst. The very low platinum content of the catalyst, coupled with the very high surface area of the alumina support (approximately  $150\text{--}200\text{ m}^2\text{ g}^{-1}$ ) meant that the extent of platinum surface was lower than that of the alumina by a factor greater than 100. Consequently, the chemisorption had to be very selective, and it was necessary to demonstrate that the chemisorption on the platinum could be determined reliably. The work of Spenadel and Boudart was very convincing in this regard and enabled them to conclude that virtually all of the platinum atoms in the catalyst were surface atoms [9]. If the platinum in the catalyst were present as three-dimensional entities (crystallites or clusters), the finding of Spenadel and Boudart implied that these entities must be extremely small, with dimensions in the vicinity of 1 nm. Chemisorption investigations of others on similar catalysts led to the same conclusion regarding the very high state of dispersion of the platinum [10–12].

Thus, selective chemisorption measurements provided a way to determine the quantity  $S/M$  representing the ratio of surface atoms  $S$  to total atoms  $M$  for the platinum component of the catalyst. Boudart subsequently introduced the term dispersion in referring to this quantity [13]. By employing a suitable value for the number of platinum atoms per square centimeter of metal surface, say  $1.10 \times 10^{15}$  (the average of the values for the (100), (110), and (111) crystallographic planes), one can estimate the surface area of the platinum component of the catalyst [1,9]. For a reaction occurring on the platinum, it is then possible to determine the reaction rate per square centimeter of platinum surface. Some forty years ago Sinfelt and coworkers made such a rate determination for the dehydrogenation of methylcyclohexane to toluene on a platinum reforming catalyst containing only 0.3 wt.% platinum [1]. At that time, very few data on rates per unit of metal surface area were available for any supported metal catalyst, let alone one with such a

low metal content. For catalysts with higher metal loadings, some results had been reported in the 1950s for the hydrogen–oxygen reaction on silica supported platinum [14] and for the ethylene and benzene hydrogenation reactions on various supported metals [15].

The rate of methylcyclohexane dehydrogenation per square centimeter of platinum surface given in the 1960 paper of Sinfelt et al. [1] was the first reported value of a rate per unit surface area for a reaction occurring on the highly dispersed platinum clusters in a reforming catalyst. It was a measure of the intrinsic dehydrogenation activity of the platinum, a quantity of fundamental importance in the characterization of the bifunctional platinum-alumina system. After the publication of this result, many similar results of investigations of other reactions on supported metals by Sinfelt and coworkers [16–25] and by Boudart and coworkers [26,27] were reported during the following decade. Eventually, it became common practice for research workers studying the catalytic properties of supported metals to obtain and report reaction rates per unit metal surface area, or alternatively, per surface metal atom. Boudart has introduced the term “turnover frequency” for the rate per surface metal atom [28], following the well-known practice in enzyme catalysis of referring to the rate per catalytic site as the turnover number [29]. This quantity provides one with a direct measure of the rate at which a catalytic cycle turns over. It has the virtue of telling us *how well* a catalyst is doing while at the same time reminding us of *what* it is doing. Although a turnover frequency for methylcyclohexane dehydrogenation was not explicitly reported in the 1960 paper of Sinfelt et al. [1], its value is actually determined more readily from the data than the rate per unit of surface area, since the latter requires information on the density of platinum atoms in the surface of a crystallite or cluster of the metal.

In the present paper, the turnover frequency is reported explicitly. Its dependence on reaction conditions is considered with the aid of the rate expression given in the 1960 paper. The rate expression in that paper was determined over a range of temperatures substantially lower than the temperatures commonly employed in catalytic reforming. Since the reaction rates were much lower at the lower temperatures, the possibility of a diffusional limitation was decreased greatly. This made it easier to study the true kinetics of the reaction, which had some intriguing features.

The interpretation of these features provided a sufficiently interesting theme for the entire 1960 paper. A matter such as the applicability of the rate expression at catalytic reforming temperatures departed from this theme and was not addressed. However, this matter is clearly of interest in the catalytic reforming process and will, therefore, be considered here as part of our discussion of turnover frequencies.

## 2. Turnover frequencies in the temperature range 588–645 K

The catalyst used in obtaining the kinetic data on methylcyclohexane dehydrogenation contained 0.3 wt.% platinum, which had a dispersion very close to 1.0 as determined by hydrogen chemisorption. A value of  $276 \text{ m}^2 \text{ g}^{-1}$  was given for the surface area of the platinum component of the catalyst in the original 1960 paper [1]. Since the surface area of the alumina support was  $155 \text{ m}^2 \text{ g}^{-1}$ , we see that the platinum covered about 0.5% of the alumina surface. Assuming a pore volume of  $0.4 \text{ cm}^3 \text{ g}^{-1}$  for the alumina [30,31], we calculate an average pore diameter of  $104 \text{ \AA}$ . Since the skeletal density of alumina is approximately  $3.5 \text{ g cm}^{-3}$  [30], the porosity is about 0.58. A rough view of the catalyst is therefore one in which 1 nm clusters of platinum are present in 10 nm pores of alumina.

The rate  $r$  of dehydrogenation of methylcyclohexane to toluene on the catalyst can be expressed as a turnover frequency  $v_t$ . In the temperature range of 588–645 K, its dependence on the methylcyclohexane partial pressure  $p_M$  is given by the equation

$$r = v_t = \frac{k' b p_M}{1 + b p_M} \quad (1)$$

where  $k'$  and  $b$  are temperature dependent parameters [1]. The temperature dependencies are given by the expressions

$$k' = 4.2 \times 10^{11} \exp\left(\frac{-33,000}{RT}\right) \text{ s}^{-1} \quad (2)$$

$$b = 2.1 \times 10^{-10} \exp\left(\frac{30,000}{RT}\right) \text{ atm}^{-1} \quad (3)$$

where  $R$  is the gas constant ( $1.99 \text{ cal mole}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature in K.

The rate data which provided the basis for Eqs. (1)–(3) were obtained at methylcyclohexane partial pressures in the range of 0.07–2.2 atm and at hydrogen partial pressures ranging from 1.1 to 4.1 atm. No effect of hydrogen partial pressure was observed, which is apparent from Eq. (1). As is customary in catalytic reforming the hydrogen was always present in excess to inhibit formation of carbonaceous residues on the catalyst surface. This made it possible to avoid a decline in catalytic activity of the platinum during the measurements. The rate data were obtained at conversion levels far lower than those corresponding to thermodynamic equilibrium, so that the effects of the reverse reaction could be neglected.

An interpretation of Eq. (1) was presented in the original paper on the kinetics [1]. It was concluded that the kinetics at low conversion levels far removed from equilibrium were best described in terms of a sequence of irreversible reaction steps in which adsorption equilibria were not established between hydrocarbon species in the gas phase and on the surface. Eq. (1) was obtained by simply equating the rate of the initial methylcyclohexane adsorption step to the rate of the final toluene desorption step. The parameter  $k'$  in Eq. (1) was then identified with the rate constant for toluene desorption while the parameter  $b$  was identified with the ratio of the rate constants for the methylcyclohexane adsorption and toluene desorption steps. The quantity  $33,000 \text{ cal mole}^{-1}$  in Eq. (2) was then interpreted as the activation energy for toluene desorption while the quantity  $30,000 \text{ cal mole}^{-1}$  in Eq. (3) was interpreted as the difference between the activation energies for toluene desorption and methylcyclohexane adsorption steps.

The reasons for abandoning the common assumption of adsorption equilibrium with regard to the hydrocarbon species in the interpretation of the rate equation were discussed in the original paper on the kinetics [1] and will not be repeated here. In the present paper, we simply use Eq. (1) with appropriate values of the parameters  $k'$  and  $b$  to calculate turnover frequencies for the reaction. In particular, we are interested in the temperature dependence of the turnover frequency.

At methylcyclohexane partial pressures high enough for Eq. (1) to exhibit zero-order behavior, the turnover frequency  $v_t$  is simply equal to the parameter  $k'$ . At a temperature of 588 K, it has the value  $0.23 \text{ s}^{-1}$ . The corresponding rate per unit area of

Table 1  
Turnover frequencies for methylcyclohexane dehydrogenation on 1 nm Pt clusters

Temperature (K)	Turnover frequency $v_t$ ( $\text{s}^{-1}$ ) <sup>a</sup>
588	0.23
617	0.84
645	2.7

<sup>a</sup> All turnover frequencies are for methylcyclohexane partial pressures high enough for zero-order kinetics to be observed; i.e.  $v_t = k'$  in Eq. (1) of the text.

platinum surface is  $2.6 \times 10^{14} \text{ molecules s}^{-1} \text{ cm}^{-2}$ , as reported for the first time some 40 years ago [1]. The effect of temperature on the turnover frequency is shown in Table 1.

The value of a reasonably thorough investigation of the kinetics of a reaction at conditions ideal for such an investigation, even when such conditions are well removed from those of most practical interest, can be illustrated by the usefulness of Eq. (1) in making estimates of rates at realistic catalytic reforming conditions. This matter is considered in the following section of the paper.

### 3. Turnover frequency at reforming conditions

We now examine the capability of Eq. (1) to give a value for the rate of methylcyclohexane dehydrogenation to toluene at typical reforming conditions, namely, a temperature of 773 K, a total pressure of 21 atm, and a hydrogen to methylcyclohexane mole ratio of 5/1. The corresponding methylcyclohexane partial pressure is one-sixth of the total pressure, i.e. 3.5 atm. Applying Eq. (1) with values of the parameters  $k'$  and  $b$  from Eqs. (2) and (3) at a temperature of 773 K, we obtain a turnover frequency of  $37 \text{ s}^{-1}$ . To compare this value with experimental data on the rate of the reaction at the designated conditions, we calculate the reaction rate per unit mass of catalyst corresponding to the turnover frequency. We obtain a value of 2.0 moles of toluene formed per hour per gram of catalyst. An experimental value of 1.4 in the same units was reported in a paper by Krane et al. for the same catalyst many years ago [32].

The experimental rate at 773 K may have been subject to a diffusional limitation, while the rate obtained by the extrapolation of the lower temperature data was

Table 2  
Comparison of turnover frequencies for dehydrogenation of methylcyclohexane and cyclohexane on 1 nm Pt clusters

Reaction	Turnover frequency $v_t$ ( $s^{-1}$ ) <sup>a</sup>
Cyclohexane $\rightarrow$ Benzene + Hydrogen	1.6 <sup>b</sup>
Methylcyclohexane $\rightarrow$ Toluene + Hydrogen	0.2 <sup>c</sup>

<sup>a</sup> Temperature 588 K, total pressure 1 atm and hydrogen to hydrocarbon mole ratio 5:1.

<sup>b</sup> Calculated from data of Cusumano et al. [33].

<sup>c</sup> Calculated from data of Sinfelt et al. [1].

free of this complication. A value of 0.7 for the catalyst “effectiveness factor” (or fraction of catalyst surface available) in the experimental rate measurement would account for the modest discrepancy between the measured value and the value obtained from Eqs. (1)–(3). For comparison, we estimate an effectiveness factor of 0.5 at 773 K from the pore volume and surface area of the alumina.

#### 4. Comparison of turnover frequencies for methylcyclohexane and cyclohexane dehydrogenation

Data reported by Cusumano et al. [33] for the rate of dehydrogenation of cyclohexane to benzene on a platinum on alumina catalyst at 588 K permit a direct comparison of the turnover frequency with that for methylcyclohexane dehydrogenation. Comparisons of reactivities for members of a homologous series are frequently not available in heterogeneous catalysis, and it is useful to make them, whenever existing data make it possible. The platinum content of the platinum-alumina catalyst used by Cusumano et al. contained 2 wt.% platinum, with a platinum dispersion approaching 1.0 as determined by hydrogen chemisorption. At a total pressure of 1 atm and a hydrogen to cyclohexane mole ratio of 5/1 (cyclohexane partial pressure equal to 0.17 atm), the rate of dehydrogenation at 588 K was reported to be 0.59 mole  $h^{-1}g^{-1}$  of catalyst. From this value, we calculate a turnover frequency for comparison with the turnover frequency for methylcyclohexane dehydrogenation determined from Eq. (1) at the same temperature and reactant partial pressure. The turnover frequencies are compared in Table 2. The calculation of the value for methylcyclohexane dehydrogenation did not require an extrapolation of Eq. (1) beyond the

conditions covered in the original investigation of the kinetics. We find cyclohexane to be eightfold more reactive than methylcyclohexane.

#### 5. Concluding remarks

The preparation of this paper revived many fond memories that the writer has of the early years of his long friendship with Michel Boudart. It is a real pleasure to acknowledge the important influence that Michel had on the early work of the writer on the kinetics of hydrocarbon reactions on platinum reforming catalysts.

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