

Heterogeneous Catalysis of Iso-Octane over Cation Exchanged Mordenite Surfaces

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This study concerns about catalytic cracking of iso-octane over cation (Cd^{2+} , Ca^{2+} and La^{3+}) exchange mordenites. It deals with mordenite shape selectivity and with kinetics of this catalytic reaction. The striking feature was that over the region of cracking temperature investigated, 523–665K, the yield of isobutene was predominant, relative to that of larger or smaller carbon chain(s). This permits kinetic analysis of the heterogeneous catalytic system in terms of the modified pulse-version microcatalytic chromatography. The observed activation energy (E_a , KJ mol^{-1}) was found to be 46 for Cd-M, 57 for Ca-M and 59 for La-M, respectively.

Introduction

Since the advent of petrochemical industries about 60 years ago, hydrocarbon cracking technology has been innovated, primarily for higher recovery of gasoline range hydrocarbons from crude oils.^{1,2} In late 1950s dramatic improvement was made by the introduction of zeolite cracking catalysts.³ This was largely indebted to the pioneering efforts of Barrer, Breck and many others.³⁻⁵ In recent years zeolite catalysis has been extended to exploration of alternative energy resources, e.g. methanol conversion into gasoline, coal liquefaction and to improvement of fuel efficiency.^{2,6,7} Studies on catalytic crackings of hydrocarbon molecules are perspective for this approach. In this work, cracking behaviours of iso-octane over cation (Cd^{2+} , Ca^{2+} and La^{3+}) exchange mordenites were investigated by means of the pulse-version microcatalytic chromatography.^{8,9} The purpose of this study is two-fold: to see the effects of exchange cation species on hydrocarbon cracking over mordenites and to investigate into the nature of mordenite-catalyzed reactions.

Experimental

Table 1 shows all the mordenite catalysts in use. They were prepared by ion exchange from a synthetic variety of "large port" Zeolon 100 Na, supplied by the Norton Co.¹⁰ Cation exchange was carried out at a reflux temperature in a batchwise mode.¹¹ In a typical exchange, 5.0 g of the parent compound was dispersed in 200 ml of a cation solution (0.02M $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1M $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.1M $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, respectively). This was stirred under a reflux condenser for 3 h. At the end of this process, the suspension was filtered and washed with de-ionized water. For higher cation loadings, the same exchange process was repeated. When the final filtrate became negative to residual anion testings, e.g. $\text{AgCl} \downarrow$, the filter-cake was dried at 105°C and conditioned to constant humidity of saturated Ca (NO_3)₂ solution prior to further use. For microcatalytic experiments the conditioned powders were pelletized under pressure of 5×10^8 Pa for 5 min. By subsequent crushing and sieving the uniform size fractions of 35–45 mesh were collected for use as catalyst.

2,2,4-Trimethyl pentane, iso-octane, was of research

TABLE 1: List of Mordenite Catalyst in Use

Catalyst	Structural Formula	Degree of exchange
Ca-M	$(\text{CaO})_{3.46}(\text{Mg}_2\text{O})_{0.54}(\text{Al}_2\text{O}_3)_4(\text{SiO}_2)_{41.30}$	87 %
Cd-M	$(\text{CdO})_{2.93}(\text{Na}_2\text{O})_{1.07}(\text{Al}_2\text{O}_3)_4(\text{SiO}_2)_{41.30}$	75
La-M	$(\text{La}_2\text{O}_3)_{1.05}(\text{Na}_2\text{O})_{0.41}(\text{Al}_2\text{O}_3)_4(\text{SiO}_2)_{41.30}$	78

grade, ex. BDH, and used after its nominal purity was confirmed chromatographically. All the other chemical reagents were of pure grade commercially available.

Cracking experiments were carried out by means of the modified precolumn technique as described in ref. 9. A gas chromatograph such as Packard Model 427 was used under the following operational conditions: TCD at 350°C, 0.23cm I.D. \times 100 cm L. glass column, packed with Apiezon L on Chromosorb W, column temperature at 90°C, helium as carrier gas (uncorrected flow rate $\sim 15\text{cm}^3 \text{min}^{-1}$), pulse size of 0.5 μl and 0.050g of catalyst (LOI basis). This gave satisfactory resolutions for the reactant/product component species involved.

Catalytic activity was measured by enumeration of component peak areas, relative to those of reference material (dry air). Product species were identified by means of chromatographic method, using the Kovats index^{12a} and mass spectroscopic methods, using a series of fragmentation patterns of reference hydrocarbon gas(es).^{12b} For convenience this was carried out in such a way that each component, chromatographically separated, was trapped at the exit of detector and then analyzed in comparison with calibration gas mixtures.¹³ Catalyst was renewed regularly, once every 10 pulses injected. A blank run was carried out with glass beads having comparable particle sizes.

Result and Discussion

Under the experimental conditions as described in the above, crackings of iso-octane over cation-exchanged zeolite surfaces were conducted at different temperatures (cf, Table 3). Typical microcatalytic chromatograms observed at 612K by reference to air peak at 53 s show two (2) well-resolved peaks of usual appearance at retention times of 59 and 137 s, respectively. These correspond to iso-butene and iso-octane, respectively. A poorly resolved shoulder peak was also found near 90 s, which corresponds to n-butene.

In order to obtain chromatograms of reasonable symmetry the size of reactant pulse and weight of catalyst need to be adjusted. Otherwise, the shape of the elution peak and the yield of product were inadequate for quantitative evaluations. Product analysis showed that at an experimental sensitivity there was no detectable product below 523K. At temperatures between 523 and 665 K there formed a single product. This was identified as *iso*-butene. At temperatures beyond 665K the product distribution was of complex nature, yielding several product species. In this case the kinetic interpretation was no longer simple due to irregular variations of individual contributions. In summary, over the range of temperatures investigated the conversion of *iso*-octane into *iso*-butene over mordenite catalysts occurred in an exclusive manner. Formation of other product species having more or less numbers of carbon atoms was found to be minor. To a first approximation appearance of spurious species was tacitly ignored for kinetic analysis according to the equation⁹:-

$$\ln \left[\frac{F^0}{m} \ln \left(1 + \frac{X}{Q} \right) \right] = \ln A' - \frac{E_a}{RT} \quad (1)$$

where F^0 = corrected flow rate of carrier gas at STP
 m = mass of catalyst in g, X = product molecules in mol,
 Q = reactant molecules in mol, A' = constant, E_a = activation energy (apparent) in $\text{KJ}\cdot\text{mol}^{-1}$, T = absolute temperature.

Further, 1st order relation was tested by the relation:-

$$\ln \left(1 + \frac{X}{Q} \right) = \frac{\alpha}{F^0} + \beta \quad (2)$$

where α and β are constants, other symbols as defined in the above.

According to eqn. 1, plots of $\ln \left[\frac{F^0}{m} \ln \left(1 + \frac{X}{Q} \right) \right]$ versus $\frac{1}{T}$ were made for each catalytic system as shown in Figure 1. At constant flow rates all the resulting plots were fairly linear over the region of experimental temperatures. From the slope of this relationship the values of E_a were calculated, which are given in Table 2. The per cent of conversions by weight observed as function of temperature are shown in Table 3. Correlation according to eqn 2. also appeared to be linear which supported 1st order relation with respect to the catalysate used.

In order to improve fuel efficiency or 'octane rating', there are more than three ways to achieve it²⁻⁴:

(i) by modifying engine designs with respect to higher compression ratio,

(ii) by catalytic reforming through disproportionation, dehydrogenation, chain branching and/or aromatization,

(iii) by simulating 'gasoline' from blending of methanol, toluene, butanol, turpentine and tetralin.

From the aspects of catalytic chemistry, the second point above has been a subject of much attention.

In thermal cracking it has been stated that the skeletal isomerization is favoured at lower temperatures, whereas

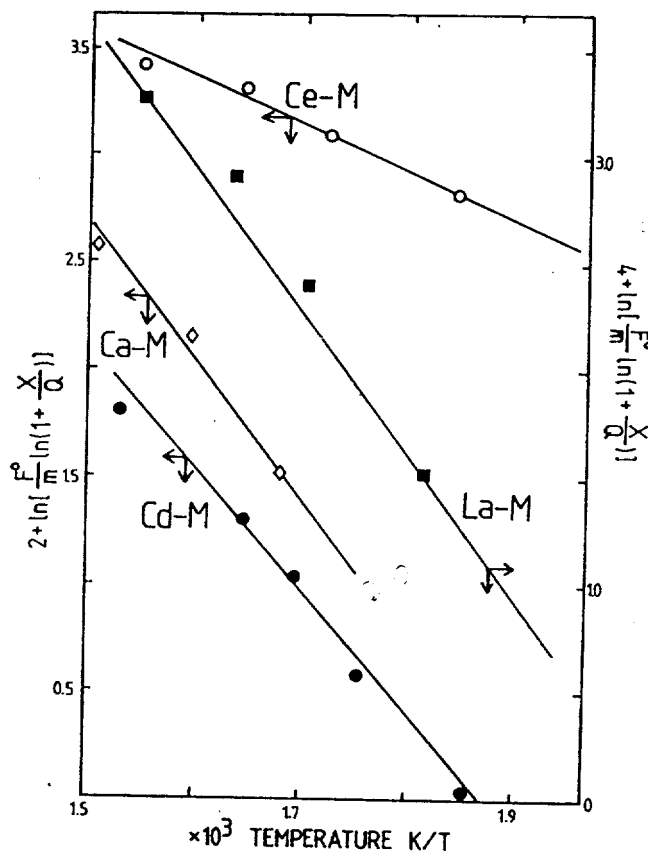


Figure 1. Temperature dependence of Arrhenius-type plots in cracking of *iso*-octane over mordenites ($F^0 = 9.8 \text{ cm}^3 \text{ STP min}^{-1}$).

TABLE 2: Apparent Activation Energies (E_a) at Regions of Temperatures as Indicated

Catalyst	Cd-M	Ca-M	La-M
Temp. Range, K	539-646	557-665	523-645
E_a , $\text{KJ}\cdot\text{mol}^{-1}$	46	57	59

TABLE 3: Temperature Dependence in Catalytic Conversion of *iso*-Octane over Mordenite Catalysts

Cd-M		Ca-M		La-M	
Temp. K	Conversion % by wt.	Temp. K	Conversion % by wt.	Temp. K	Conversion % by wt.
539	13.0	557	22.3	523	4.8
569	22.3	594	46.1	550	8.0
590	32.2	612	69.0	587	17.9
607	39.7	665	83.3	612	28.4
645	52.2	—	—	645	38.5

cyclization or aromatization is promoted at higher temperatures.¹⁴⁻¹⁶

From the thermodynamic points of view the cracking of hydrocarbons is endothermic and hence the cracking itself should be facilitated at an elevated temperature. Therefore, at a cracking temperature (usually under pressure) the two effects are expected to occur concurrently. This will result in a range of product distribution. By a proper choice of cracking catalyst the mode of chain cleavage may be controlled so that selectivity for particular product species should

be enhanced. In the present case, there formed a single product species of *iso*-butene (*vide supra*) predominantly over the mordenite catalysts, despite the entire difference in exchanged cations per se. Implication is therefore that unique cracking mechanism is operative, regardless of cation species present in mordenite cavities. This is regarded as mordenite shape selectivity, the experimental temperatures so adjusted being optimal to this effect.

It is also surprising that the end-product was an unsaturated hydrocarbon. This indicates that the catalytic cracking accompanies dehydrogenation, most likely during the passage through the mordenite main channels. There was no indication of aromatization or cyclization. It has been postulated that chain cleavage occurs either through formation of carbocation or through formation of free radicals². Since there was no evidence for the free radical mechanism such as lower molecular weight species like CH₄, the present cracking reaction is attributed to the carbocation type. For expediting the carbocation formation the surface acid sites are undoubtedly responsible.¹⁷

In all probability, the skeletal cleavage may be initiated through protonation, hydride ions being subsequently abstracted and transferred in mordenite pores. Since quaternary carbon atoms in branched hydrocarbon molecules are prone to protonic attacks, *iso*-octane would be susceptible to β -scission, yielding a C₄-hydrocarbon^{16,18}

As to the origin of surface acidity, the active loci of Brønsted type are considered to be of prime importance, while that of Lewis type is complimentary.^{2,5} In the present case this can be accounted for in such a way that hydrocarbon molecules are coordinatively adsorbed on Lewis acid sites and this facilitates molecular accessibility to the Brønsted sites.¹⁹

Although the characteristic properties of individual cations were not directly demonstrated by the product distribution, correlation between cation activity and catalytic activity would be made possible, at least in qualitative manners. This is because the surface acidity is related to the electrostatic field strengths of the exchange cations.²⁰⁻²³ The trend is shown by the fact that the energy of activation (apparent) decreases with increase in ionization potential (eV) of the exchange cations.²² For example, the values of E_a for La-M, Ca-M and Cd-M were 59, 57 and 46 KJ·mol⁻¹, respectively. However, further elaboration of this point would not be attempted until sufficient data are to be observed in this regard. In addition, there is no unified consensus as to the subject how the mordenite channels can exert catalytic activity on the molecules of sterically incompatible sizes. In general, contradictory evidence is quite commonly encountered in use of zeolite catalysts, whereby the guest molecules of larger than the aperture sizes undergo catalysis, especially in mordenite sieves (free aperture 0.62 nm in diameter).

According to Mortier et al²⁴ the exchange cations such as Ca²⁺ in mordenite pores are mobile, being possibly migrated into the main channels. This is stated to occur when the degrees of exchange and of hydration reach certain critical levels. For La³⁺ exchange faujasite-type zeolite, analogous

explanation was offered, viz. sharp increase in acidity only appears beyond approximately 20% cation exchange.²⁵

In this work, all the cation exchange was carried out in an exhaustive way (*vide supra*). Since the branched chain molecule of *iso*-octane has a critical diameter of 0.6 nm, it may experience fair resistance to tubular passage through the cation-distributed channel spaces. Without doubt, the reactant molecules will be rejected from entrance to the side pockets.

Further, diffusion of *iso*-octane through the mordenite channels is believed to be about 100 times slower than that of the linear isomer, *n*-octane.²⁶ When the same ratio is assumed for the catalytic activity occurring on the internal and external surfaces, the catalytic effects of the external surfaces would be negligible. Therefore the cracking of reactant molecules should occur at the active centres very close to the external surfaces, e.g. near the apertures, rather than in deep channel spaces. Further transformation such as olefinization may then be taken place during the channel passages. In this connection, it may be relevant to point out that depletion in pressure or thermal convection may prevail near the entrance of the main tunnels. The active centres in this vicinity may initiate primary chain cleavage, giving rise to carbocations. Otherwise, the structure reactivity correlation is hardly rationalized.

Certainly this view is an oversimplification and other factors, such as molecular flexibility, silanol groups in crystal defects, would also play an important role in this regard. However the latter is beyond the scope of the current discussion. Desorption of products from the channel space may be explained in a similar way. The cracking mechanism of *iso*-octane is proposed as depicted in Figure 2.

From the evidence alone, it may be sufficient to conclude that over the cation exchange mordenite catalysts the cracking of *iso*-octane is subjected to β -scission, being highly selective for olefinic molecules. This is regarded as phenomenon of two-stage surface interaction, viz. primary chain cleavage at apertures and secondary alkenization during channel passage.

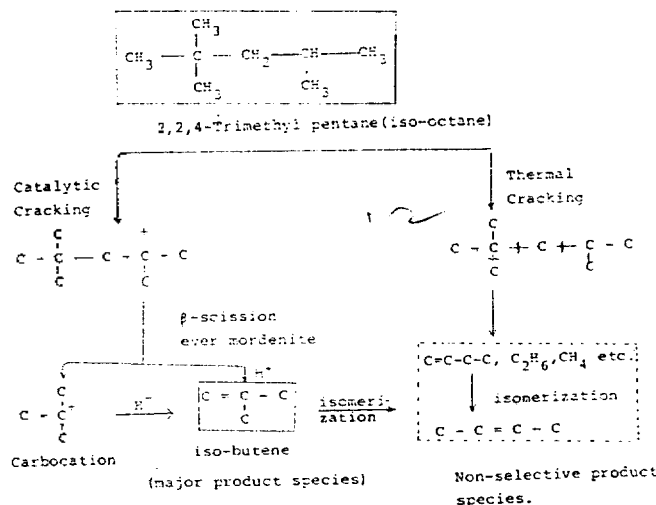


Figure 2. Possible mechanism for cracking of *iso*-octane.

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The Anomalies of Supercooled Water

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The anomalous behaviors of supercooled water are explained by using a two-solid-like structure model in which an equilibrium is assumed between open structures and closed structures. Besides these structures, small fraction of monomer exists in liquid water. The anomalies of liquid water are classified into two groups: structural and energetic. The structural anomalies appear in enlarged fashions in a supercooled state where the free volume is small.

Introduction

Water is an unusual liquid which has the various anomalous properties, while it is representative as a liquid on earth. Up to the present, scientists have continued many experimental researches on liquid water without ceasing to add theoretical explanations and predictions but they are not satisfactory

for understanding the structure. Theoretical views for models of water group are classified into two directions. In 1957, Pople¹ suggested a bent bond model in which hydrogen bonds (H-bonds) connecting adjacent water molecules were bent to yield a continuous distribution of bond angles and energies. This model gave a little explanations for the anomalous properties of water than reproduced the Morgan and Warren's X-ray diffraction pattern.² However, continuum theories³ have been favored to scientists due, maybe, to the fact that so is the conventional concept of H-bonding

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