Conversion of Cyclohexene over Y-Zeolites: A Model Reaction for Hydrogen Transfer

W-C. Cheng and K. Rajagopalan

W. R. Grace & Co.–Conn., Davison Chemical Division, 7379 Route 32, Columbia, Maryland 21044

Cyclohexene was reacted at 523°K over Y-zeolite catalysts with a unit cell constant in the range of 2423 to 2448 pm. The selectivity toward the hydrogen transfer products (cyclohexane plus methylcyclopentane) increases with the unit cell constant, while the selectivity toward isomerization products (methylcyclopentene plus methylcyclopentane) remains constant in the unit cell constant range of 2448 to 2427 pm and increases as the unit cell constant decreases to 2423 pm. The results are rationalized on the basis of acid site density and the nature of the reactions. Hydrogen transfer, being a bimolecular reaction, is favored by a high-acid site density, while isomerization of olefins, being a unimolecular reaction, is not dependent on site density but only on strength of the acid site. Thus, reaction of cyclohexene can be used as a test reaction to measure hydrogen transfer properties of acid catalysts. The relevance of these results to product quality from catalytic cracking is discussed. © 1989 Academic Press, Inc.

INTRODUCTION

Increasing the octane of FCC gasoline is a goal of many refiners. One of the keys to increasing FCC gasoline octane number is to increase the rate of cracking relative to the rate of hydrogen transfer on the catalyst (*1, 2*). Numerous studies have been devoted to understanding the nature of hydrogen transfer reactions on zeolites (*3–6*). This subject has been reviewed recently by Chen and Haag (*7*). The object of this work is to develop a model compound reaction to characterize the hydrogen transfer properties of solid acid catalysts and to relate these properties to the performance of the catalysts in gas oil cracking. The disproportionation of cyclohexene to benzene and cyclohexane is a frequently studied hydrogen transfer reaction in metal catalysis (*8*). This is an interesting reaction as the reactant can act as both hydrogen donor and acceptor. Recently, Magnoux *et al.* (*9*) have studied the reaction of cyclohexene at low pressure (5 kPa cyclohexene partial pressure) on ultrastable Y-zeolite. They determined the effect of temperature on the

product selectivity. In the present study we have explored the effect of acid site density of zeolite Y on the product distribution.

EXPERIMENTAL METHODS

Catalyst Preparation and Characterization

Low soda Y-zeolites having a rare-earth loading of 0 to 13 atoms per unit cell were prepared by carrying out ion-exchange and calcination processes on each of two commercially available (Davison Chemical Division, W. R. Grace & Co.) faujasite zeolites (NaREY and Z-14US). Details of the ion-exchange methods have been described by Rajagopalan and Peters (*10*). Properties of four zeolites are shown in Table 1.

The zeolites were mixed intimately with an alumina sol binder and kaolin clay diluent and spray-dried to produce spherical catalyst particles having a diameter range from 20–140 μm. Zeolite content of these catalysts was varied from 15 to 40 wt% to achieve catalysts of comparable cracking activity after hydrothermal treatment. The catalysts were steamed in a fluidized bed at

TABLE 1

Properties of Zeolite Catalysts

Zeolite properties				
RE/unit cell	13.0	4.2	2.1	0
wt% zeolite in catalyst	15	27	36	40
Catalyst properties				
wt% Al_2O_3	43.3	42.6	43.3	43.3
wt% RE_2O_3	2.69	1.77	1.14	0.07
wt% Na_2O	0.23	0.19	0.41	0.26
BET surface area/m^2 g^{-1}	142	200	286	273
Nitrogen pore volume/cm^3 g^{-1}	0.10	0.21	0.21	0.21
Bulk density/g cm^{-3}	0.82	0.78	0.69	0.73
Average particle size/μm	72	54	64	70
After hydrothermal treatment				
BET surface area/m^2 g^{-1}	69	128	180	172
Unit cell constant/pm	2448	2431	2427	2423
Al/unit cell[a]	33.4	13.8	9.2	4.6
Al/unit cell[b]	27.8	8.7	4.2	0

[a] Calculated as 1.152 × (unit cell − 2419) (11).
[b] Calculated as 1.124 × (unit cell − 2423.3) (12).

1088 K and a steam pressure of 101 kPa for a period between 1 and 6 h to simulate aging in a commercial FCC unit.

Properties of the fresh and steam-deactivated catalysts are shown in Table 1. The unit cell constants of the zeolites in the steamed catalysts as determined by X-ray diffraction (ASTM procedure D-3942-80) varied between 2423 to 2448 pm. This corresponds to an aluminum site density range of 4.6 to 33.4, as calculated by the correlation of Breck and Flanigen (11) or 0 to 27.8 as calculated by the correlation of Fichtner-Schmittler et al. (12).

Catalyst Evaluation

Cyclohexene reactions were carried out using a modified fixed-bed ASTM D-3907-80 microactivity procedure. The reactor was operated at atmospheric pressure and 523 K. For a given catalyst, conversion was varied by varying the catalyst to feed ratio (C/F) while maintaining a constant catalyst residence time of 75 s. The gaseous and liquid products were analyzed by gas chromatography. The carbonaceous deposit on the spent catalyst was measured by carbon determinator WR-12 (Leco Corporation, St. Joseph, MI). The product mass balance was typically >95%, and was normalized

for reporting. Cyclohexene (Aldrich Gold Label 99+% purity) was used without further purification.

RESULTS AND DISCUSSION

Catalyst Activity and Product Distribution

The conversion of cyclohexene as a function of the catalyst to feed ratio for the four catalysts is shown in Fig. 1. The catalyst containing the highest unit cell zeolite and the lowest zeolite content had a lower activity than the other three. This is due to more extensive zeolite destruction of this sample during steaming. However, the range of conversion for all the catalysts is between 10 and 30 wt%.

The liquid reaction products were analyzed by GC/mass spectroscopy. The major components consisted of a hydrogenated product (cyclohexane), isomerized products (1-, 2-, and 3-methylcyclopentene), isomerized and hydrogenated product (methylcyclopentane), and dimerized C_{12}'s. Minor amounts of alkylated products (dimethylcyclopentane, dimethylcyclopentene, methylcyclohexane and methylcyclohexene) were observed. The concentration of benzene in the product was very low. Low levels of benzene were also observed by Magnoux et al. (9).
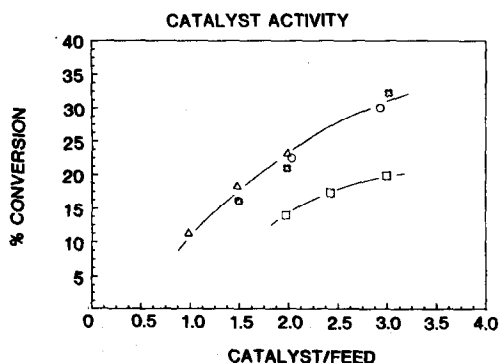
CATALYST ACTIVITY

FIG. 1. Conversion of cyclohexene as a function of catalyst to oil ratio over Y-zeolite catalysts of unit cell size: (□) 2448 pm, (○) 2431 pm, (⊠) 2427 pm, (△) 2423 pm at 523 K and 75 s contact time.
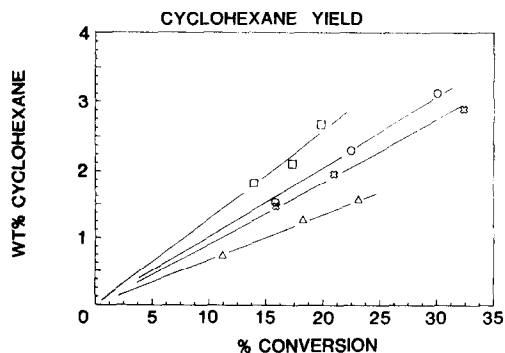
CYCLOHEXANE YIELD

FIG. 2. Cyclohexane yield as a function of cyclohexene conversion over Y-zeolite catalysts of unit cell size: (□) 2448 pm, (○) 2431 pm, (☒) 2427 pm, (△) 2423 pm.

METHYLCYCLOPENTANE YIELD

FIG. 3. Methylocyclopentane yield as a function of cyclohexene conversion over Y-zeolite catalysts of unit cell size: (□) 2448 pm, (○) 2431 pm, (☒) 2427 pm, (△) 2423 pm.

Hydrogen Transfer and Isomerization

The yield of cyclohexane as a function of cyclohexene conversion is shown in Fig. 2. As the yields follow a straight line to the origin, cyclohexane can be characterized as a primary stable product (13). This suggests that cyclohexane is formed directly by hydrogen transfer to the reactant cyclohexene. The initial selectivity, given by the slope of the lines, increases as the unit cell constant and the site density of the zeolite increases. This is the expected result as hydrogen transfer is a bimolecular reaction (1, 7, 14) and is facilitated by the proximity of sites.

The yield of methylcyclopentane as a function of cyclohexene conversion is shown in Fig. 3. The extrapolated yield curves show a zero slope of the origin, suggesting that methylcyclopentane is a secondary stable product (13). It is formed by hydrogen transfer to methylcyclopentenes which are formed by the isomerization of cyclohexene. The yield of methylcyclopentane generally increases as the unit cell constant of the zeolite increases. The unexpectedly higher yield of methylcyclopentane on the zeolite with 2423 pm cell size is attributed to the higher initial isomerization activity of this catalyst, giving rise to a higher concentration of the intermediate methylcyclopentene.
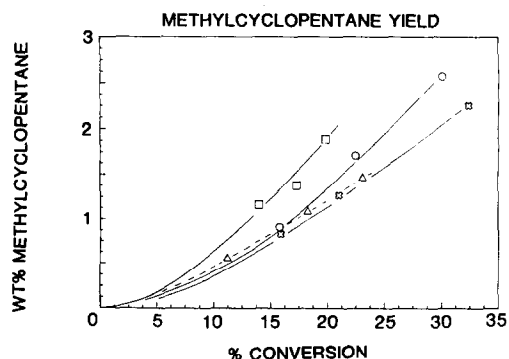
The yield of isomerization products (the sum of the methylcyclopentene isomers) as a function of conversion is shown in Fig. 4. The methylcyclopentenes are primary unstable products capable of further reacting by hydrogen transfer to form methylcyclopentane. The isomerization selectivities of the catalysts with zeolite unit cell size from 2448 down to 2427 pm were equal while that of the catalyst with a zeolite unit cell size of 2423 pm was somewhat higher. Isomerization of olefins is a unimolecular reaction (7), and should occur on all sites, including isolated sites. Thus, the yield of isomerization products should be independent of site
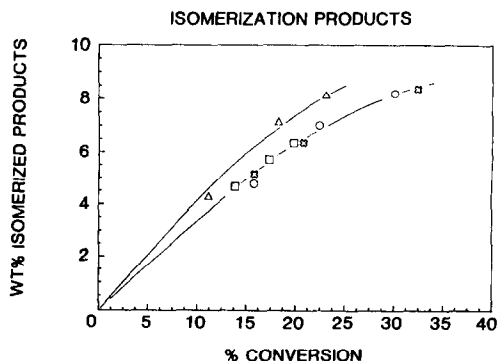
ISOMERIZATION PRODUCTS

FIG. 4. Isomerization product yield as a function of cyclohexene conversion over Y-zeolite catalysts of unit cell size: (□) 2448 pm, (○) 2431 pm, (☒) 2427 pm, (△) 2423 pm.

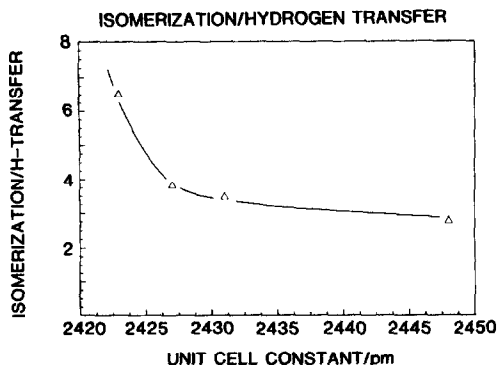ISOMERIZATION/HYDROGEN TRANSFER

FIG. 5. Ratio of the initial selectivities of isomerization to hydrogen transfer as a function of zeolite unit cell size.

density. This is observed for three of the catalysts. The higher isomerization yield of the catalyst with the lowest unit cell size may be attributed to its higher acid strength. Beaumont and Barthomeuf (15, 16) have shown that as the SiO_2/Al_2O_3 ratio of the zeolite increases, the acid site strength increases. Higher cracking activity of high SiO_2/Al_2O_3 Y-zeolite has also been reported by Magee (17) and Mirodatos and Barthomeuf (18).

The initial selectivities are given by the slopes of the yield curves at the origin. The ratio of the initial selectivities of isomerization to hydrogen transfer is a measure of the relative rates of 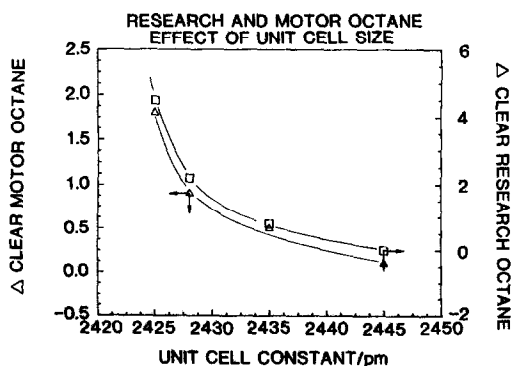unimolecular and bimolecular processes. A plot of this parameter as a function of the unit cell constant is shown in Fig. 5. The ratio of isomerization to hydrogen transfer selectivities decreases sharply as the unit cell constant increases from 2423 to 2431 pm and decreases more gradually as the unit cell constant increases beyond 2431 pm. The effect of zeolite unit cell size on FCC gasoline octane (research and motor) has been reported by Ritter et al. (2), and is shown in Fig. 6. There is a remarkable similarity in the effect of unit cell on gasoline octane and on the isomerization/hydrogen transfer ratio during the reaction of cyclohexene. In the case of gas oil cracking, as the unit cell size and the site density decreases, the rate per site of hydrogen transfer (bimolecular) decreases, while the rate per site of the cracking reaction (unimolecular) stays the same or increases due to the increase in acid site strength. This leads to a gasoline which is higher in olefin content and higher in octane quality.

C_{12}'s and "Coke"

The yield of C_{12}'s as a function of conversion is shown in Fig. 7. The C_{12}'s are the sum of cyclic olefins and cycloparaffins. The C_{12} olefins are expected to be primary products capable of being converted to the C_{12} paraffins, which are expected to be secondary and stable products. Thus, the lump sum C_{12} yields appear to lie along a straight
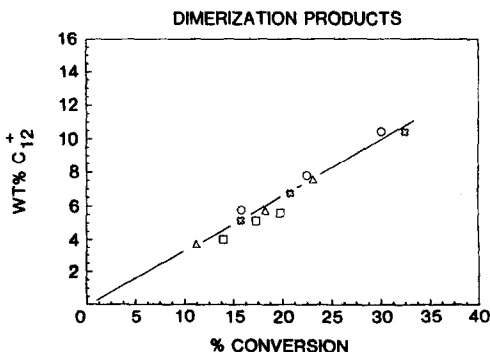
RESEARCH AND MOTOR OCTANE
EFFECT OF UNIT CELL SIZE

FIG. 6. Research and motor octane of FCC gasoline as a function of unit cell size. From Ref. (2).

DIMERIZATION PRODUCTS

FIG. 7. Dimerization product yield as a function of cyclohexene conversion over Y-zeolite catalysts of unit cell size: (□) 2448 pm, (○) 2431 pm, (✿) 2427 pm, (△) 2423 pm.
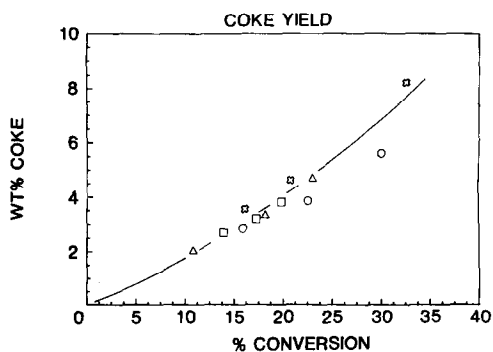
line passing through the origin. Dimerization selectivity appears to be independent of the unit cell size. This would be a surprising result since this reaction is bimolecular; however, dimerization is an electron transfer reaction and not a hydrogen transfer reaction (7). It can occur on a single site between a C_6 carbenium ion and a physisorbed or a gas-phase C_6 olefin.

The "coke" yield, shown in Fig. 8, also appears to be independent of cell size. This is unexpected since for gas oil cracking, the coke yield decreases with decreasing cell size (2). However, the measured "coke" includes polymerization products (trimers, tetramers, etc.) which are not desorbed from the catalyst at the reaction temperature of 523 K. Thus, the effect of cell size is not observed.

CONCLUSIONS

In the reaction of cyclohexene over Y-zeolites, the selectivity toward hydrogen transfer products increases as the unit cell size of the zeolite increases from 2423 to 2448 pm. The selectivity toward isomerization products does not change greatly with unit cell size from 2448 down to 2427 pm but increases as the unit cell size decreases further to 2423 pm. The ratio of the yields of isomerization products to hydrogen transfer products is a measure of the relative importance of unimolecular to bimolecular reactions. This parameter correlated very well with the research and motor octane of FCC gasoline. Thus the reaction of cyclohexene at a moderate temperature is a good model compound reaction for probing the hydrogen transfer characteristics of a solid acid catalyst.

REFERENCES

1. Pine, L., Maher, P. J., and Wachter, W. A., J. Catal. 85, 466 (1984).
2. Ritter, R. E., Creighton, J. E., Roberie, T. G., Chin, D. S., and Wear, C. C., in "Proceedings, NPRA Meeting, Los Angeles, CA, March 23–25, 1986."
3. Abbot, J., and Wojciechowski, B. W., J. Catal. 107, 451 (1987).
4. Kramer, G. M., and McVicker, G. B., Acc. Chem. Res. 19, 78 (1986).
5. Franco Parra, C., Goldwasser, M. R., Fajula, F., and Figueras, F., Appl. Catal. 17, 217 (1985).
6. Guisnet, M., in "Catalysis by Acids and Bases" (B. Imelik, Ed.), p. 283. Elsevier, Amsterdam/New York, 1985.
7. Chen, N. Y., and Haag, W. O., in "Hydrogen Effects in Catalysis Fundamentals and Practices" (Z. Paal and P. G. Menon, Eds.), p. 695. Dekker, New York and Basel, 1988.
8. Boudart, M., and Cheng, W-C., J. Catal. 106, 134 (1987).
9. Magnoux, P., Gallet, A., and Guisnet, M., Bull. Soc. Chim. Fr. 5, 810 (1987).
10. Rajagopalan, K., and Peters, A. W., J. Catal. 106, 410 (1987).
11. Breck, D. W., and Flanigen, E. M., in "Molecular Sieves" (R. M. Barrer, Ed.), p. 47. Society of Chemical Industry, London, 1968.
12. Fichtner-Schmittler, H., Lohse, U., Engelhardt, G., and Patzelova, V., Cryst. Res. Technol. 19(1), K1 (1984).
13. Corma, A., and Wojciechowski, B., Catal. Rev. Sci. Eng. 24, 1 (1982).
14. Gates, G. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," p. 39. McGraw-Hill, New York, 1979.
15. Beaumont, R., and Barthomeuf, D., J. Catal. 26, 218 (1972).
16. Barthomeuf, D., J. Phys. Chem. 83, 249 (1979).
17. Magee, J. S., in "Catalysis 1987" (J. W. Ward, Ed.), p. 303. Elsevier, Amsterdam/New York 1988.
18. Mirodatos, C., and Barthomeuf, D., J. Catal. 114, 121 (1988).