2768 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2768—2773 (1983) [Vol. 56, No. 9

Product Distribution in Degradation of Polypropylene over Silica-Alumina and CaX Zeolite Catalysts

Yoshio Uemichi,* Yasunori Kashiwaya, Masaya Tsukidate,
Akimi Ayame, and Hisao Kanoh
Department of Industrial Chemistry, Muroran Institute of Technology, Mizumoto-cho, Muroran 050

(Received March 14, 1983)

The composition of degradation products of polypropylene, especially liquid fraction, formed over silica-alumina and CaX zeolite catalysts was investigated extensively. The catalysts gave almost the same product distribution as a function of carbon number at the initial stages of the reaction. The liquid fractions were rich in the same isoalkanes and aromatics as those contained in the gasoline fraction. Most of the isoalkanes were methyl-branched, while the aromatics consisted mainly of those with one or more methyl groups. The catalytic degradations involved extensive aromatization, isomerization and hydrogen transfer as secondary reactions. The difference in catalytic behaviors between silica-alumina and CaX was most remarkable in coke deposition on the catalysts and more deposition on CaX led to greater saturation of the products. The H/C ratio of the products was regarded as a good measure for the degree of coke formation on the catalyst surfaces.

In recent years attention has been paid to the reuse of plastic wastes from the viewpoint of energy diversification, necessitating the development of processes capable of recovery as chemical resources or fuel. As the thermal degradation products of polypropylene are distributed in a wide range of carbon numbers,[1,2] the utility value of the products recovered is low, so that upgrading will be required for efficient utilization of them. On the other hand, a selective recovery of useful fractions is possible in catalytic degradation and further the product distribution is controlled more readily than the case of thermal degradation. Thus, the catalytic procedures are superior to thermal methods provided that the products are intended for resources. However, only a few investigation have been reported on catalytic degradation of polypropylene.[3–5] A great deal of emphasis is placed on the identification of the products in thermal degradation of polypropylene.[6–9] Similarly, a detailed analysis of the products is undoubted to be important also in catalytic degradation, but there has been no report on an extensive analysis of degradation products of polypropylene in the presence of acid catalysts because of complexity of the product composition. The authors have already reported the catalytic degradations of polypropylene over silica-alumina and CaX zeolite,[3] which were aimed at the formation of gaseous fractions so that the liquid fractions were characterized by gross properties such as average molecular weight, iodine number and infrared spectrum. However, it is expected that a survey of the composition of liquid fractions is very informative for clarifying the degradation mechanism, and further the survey will be a significant research for efficient utilization of the products.

From the point of view described above, the purpose of this study is to identify the degradation products, especially liquid fractions, of polypropylene over silica-alumina and CaX zeolite catalysts and to discuss the catalytic degradation mechanism.

Experimental

Apparatus and Procedures. The experiments were conducted in the same fixed-bed flow system, except that a water-cooler was connected at the outlet of a separator, as in the previous study.[3] Polypropylene sample was melted in a melter at 240 °C under an atmosphere of nitrogen. The melt of polypropylene was introduced into a reactor through a capillary of inside diameter of 2 mm. The feed rate of polypropylene was controlled by both the temperature of the capillary and the pressure of the nitrogen in the melter. They were kept constant through a run at given levels in the range of 280—320 °C and 0.3—0.4 kg/cm^2 G, respectively. Liquid products were collected in the separator at 20 min intervals. Because of high activities of the catalysts, the relatively low temperature of 477 °C was employed for catalytic degradation, rather than 526 °C which was used for the thermal degradation.

Materials. Isotactic polypropylene and silica-alumina and CaX catalysts were the same as those used in the previous study.[3] The average molecular weight of the polypropylene was 1.6×10^5 and its tacticity was characterized by pyrolysis-gas chromatographic method.[10] The catalysts were calcined before use in the air at 550 °C for 3 h and 3.0 g of each catalyst was used in a run. A reactor packed with glass beads of 3.5 mm in diameter was used in thermal degradation.

Analysis. The degradation products were analyzed by gas chromatography. Three columns, VZ-7 (5 m×3 mm i.d.), active carbon (1 m×3 mm i.d.) and OV-101 (50 m×0.28 mm i.d.), were used for the separation of components. Two methods were employed as supplementary techniques for the identification of the products. One was hydrogenation of alkenes using a column of supported palladium catalyst. The other was selective absorption of alkenes and aromatics using an absorbent column of supported mercury(II) perchlorate. The details of the two methods have been described elsewhere.[11] A splitter was independently held at 250 °C to attain reproducible splitting for the degradation products with a wide range of volatility. The peaks in a chromatogram were identified by co-injection of the products with standard materials. When pure materials were not available, the identification was based on a linear relation between boiling point and retention index. From a quantitative analysis using methylcyclohexane as internal standard, the products were found to contain nondetectable fractions under the gas chromatographic condition, and so they were summarized as high-boiling-point products (H.B.P).

Results and Discussion

The composition of the degradation products of

TABLE 1. DISTRIBUTION OF CATALYTIC DEGRADATION PRODUCTS[a]

Carbon No.	Silica-Alumina					CaX				
	Normal alkanes	Iso-alkanes	Alkenes	Aromatics	Total	Normal alkanes	Iso-alkanes	Alkenes	Aromatics	Total
H_2					0.1 (tr)[c]					tr (tr)[d]
1	0.8				0.8 (0.4)	0.9				0.9 (0.9)
2	0.4		0.5		0.9 (0.5)	0.9		0.5		1.4 (0.8)
3	1.6		9.6		11.2 (7.8)	2.6		8.3		10.9 (2.8)
4	1.8	13.6	13.1		28.5 (20.1)	3.6	19.1	8.0		30.7 (5.0)
5	1.0	10.0	10.7		21.7 (19.6)	2.1	17.1	3.9		23.1 (7.5)
6	0.4	6.7	6.5	0.3	13.9 (18.7)	1.1	11.4	1.3	0.2	14.0 (6.8)
7	0.1	2.3	2.7	2.9	8.0 (7.9)	0.4	6.0	0.2	1.1	7.7 (7.3)
8	tr[b]	1.3	0.7	3.5	5.5 (4.7)	0.2	2.5		2.3	5.0 (8.3)
9		0.6	0.2	2.0	2.8 (2.6)	0.1	0.9		1.8	2.8 (8.2)
10		0.2		1.4	1.6 (1.4)	tr	0.2		0.6	0.8 (2.0)
11		0.1		0.2	0.3 (0.1)		0.1		0.1	0.2 (1.4)
12		tr		0.3	0.3 (tr)		tr		tr	tr (0.9)
13—16					0.5 (tr)					(2.0)
H.B.P					3.8 (16.1)					2.6 (46.2)
Total	6.1	34.8	44.0	10.6	99.9 (99.9)	11.9	57.3	22.2	6.1	100.1 (99.9)

a) Distribution (wt%) obtained at the initial stages of the reaction. Reaction temperature: 477 °C, catalyst weight (W): 3.0 g, feed rate (F): 0.150 g-PP min^{-1} (PP) polypropylene. b) Trace amount of less than 0.05%. c) Distribution at 165 min after starting reaction. d) Distribution at 130 min.

polypropylene was simplified by the selective absorption of alkenes and aromatics, which resulted in a chromatogram consisting of saturated hydrocarbons only. The absorbed alkenes and aromatics were distinguished each other by the hydrogenation over palladium catalyst. The hydrogenation caused a transformation of alkenes to corresponding alkanes, although aromatics except for naphthalenes were not hydrogenated. Thus, the degradation products were classified into five groups of hydrogen, normal alkanes, isoalkanes, alkenes and aromatics. However, most of the alkenes were difficult to identify because of many possible isomers. The product distributions as a function of carbon number at the initial stages of the reaction are shown in Table 1. Both catalysts gave essentially the same distribution and the relative yield of C_3—C_6 fractions was very high. Isoalkanes were preferentially produced in C_4—C_6 fractions. The selectivity to aromatics became higher, while that to alkenes decreased, as carbon number increased. The products formed over CaX were more saturated than those over silica-alumina. The difference in the degree of saturation would be attributed to the extent of hydrogen transfer reaction. This will be described later. The normal alkane content was always smaller than that of isoalkanes and, as carbon number increased, the content of multibranched alkanes increased in proportion to the number of possible isomers. Figure 1 well illustrates these facts for the products formed over silica-alumina. Here, most of the branchings were methyl groups. CaX catalyst also gave the same distribution of alkane isomers. Further, detailed compositions of aromatics are shown in Table 2. Toluene, xylenes and trimethylbenzenes were the main aromatics. The aromatics with ethyl group were minor products and those with C_3 or C_4 alkyl group were little produced. Therefore, C_{10} aromatics in Table 2 would correspond

TABLE 2. COMPOSITION OF AROMATICS[a]

Component	Silica-Alumina	CaX
Benzene	3.5	5.3
Toluene	31.6	27.0
Ethylbenzene	2.1	2.8
Xylenes	32.0	36.5
Ethyltoluenes	3.6	7.1
Trimethylbenzenes	13.5	15.0
Tetramethylbenzenes	3.8	1.8
C_{10} Aromatics	6.7	4.0
Methylnaphthalenes	1.5	0.3
Dimethylnaphthalenes	1.8	0.3

a) Composition: mol%, reaction conditions: See Table 1.

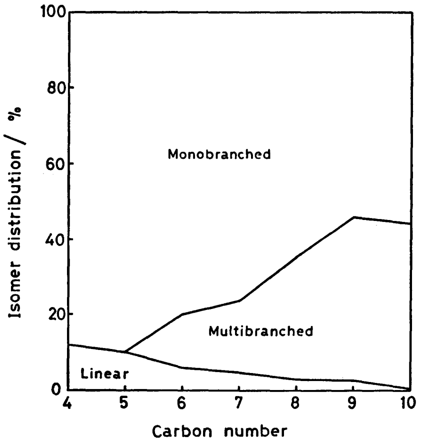

Fig. 1. Distribution of alkane isomers formed over silica-alumina.
Reaction conditions: See Table 1.

TABLE 3. COMPARISON BETWEEN ISOMER DISTRIBUTION AND THERMODYNAMIC EQUILIBRIUM

Type	Component	Isomer distribution[a]/%		Equilibrium[b]/%
		Silica-Alumina	CaX	
Alkanes	2,2-Dimethylbutane	0	0	21
	2,3-Dimethylbutane	14	12	10
	2-Methylpentane	47	49	28
	3-Methylpentane	33	30	17
	Hexane	6	9	24
Alkenes	3-Methyl-1-butene	4	4	4
	1-Pentene	5	5	5
	2-Methyl-1-butene	22	22	27
	trans-2-Pentene	15	14	14
	cis-2-Pentene	8	8	9
	2-Methyl-2-butene	46	47	41
Aromatics	1,3,5-Trimethylbenzene	24	24	23
	1,2,4-Trimethylbenzene	64	64	66
	1,2,3-Trimethylbenzene	12	12	11

a) Reaction conditions: See Table 1. b) 470 °C

TABLE 4. DISTRIBUTION OF THERMAL DEGRADATION PRODUCTS[a]

Carbon No.	Normal alkanes	Isoalkanes	Alkenes	Total	Main components
H_2				tr[b]	
1	1.0			1.0	Methane
2	2.1		1.0	3.1	Ethane
3	0.4		8.3	8.7	Propylene
4			3.5	3.5	Isobutylene
5	4.0		1.5	5.5	Pentane
6		0.3	4.8	5.1	2-Methyl-1-pentene
7			2.5	2.5	2,4-Dimethyl-1-pentene
8		0.8	1.3	2.1	4-Methylheptane
9		0.5	11.4	11.9	2,4-Dimethyl-1-heptene
10			1.0	1.0	2,4,6-Trimethyl-1-heptene
11		0.4	0.5	0.9	4,6-Dimethylnonanes (2)[c]
12			1.7	1.7	2,4,6-Trimethyl-1-nonenes (2)
13			0.8	0.8	2,4,6,8-Tetramethyl-1-nonenes (2)
14		0.2	0.2	0.4	4,6,8-Trimethylundecanes (3)
15			3.0	3.0	2,4,6,8-Tetramethyl-1-undecenes (4)
16			1.1	1.1	2,4,6,8,10-Pentamethyl-1-undecenes (3)
17—24			5.1	5.1	
H.B.P				42.9	
Total	7.5	2.2	47.7	100.3	

a) Distribution: wt%, reaction temperature: 526 °C, feed rate: 0.116 g-PP min^{-1}. b) Trace amount of less than 0.05%. c) The number of diastereomeric isomer.

to those with methyl and/or ethyl groups.

In general, isomer distribution is strongly dependent on thermodynamics. Table 3 shows the comparison between isomer distribution and thermodynamic equilibrium.[12–14] Alkene and aromatic isomers were distributed approximately in accord with the corresponding thermodynamic equilibria, whereas the distribution of alkane isomers was entirely different and the content of branched alkanes exceeded the possible thermodynamic equilibrium concentration. These results indicate that equilibria of alkene and aromatic isomers are more rapidly attained than an equilibrium among alkanes. Although each component of alkenes larger than C_5 fraction was not identified, it is expected that alkenes show a higher ratio of linear to branched hydrocarbons than do the alkanes of the same carbon number. This is because of faster saturation of branched alkenes than linear alkenes.[15]

As mentioned above, the liquid products from catalytic degradation of polypropylene contained large amount of isoalkanes and aromatics which constitute the gasoline fraction.[16] The formation of a gasoline fraction seems to be advantageous for a utilization of the products. Further, the composition of the catalytic degradation products of polypropylene over silica-alumina resembled that of polyethylene.[11] A

Table 5. Effects of contact time and reaction time on composition of the products formed over silica-alumina[a)]

Component	Contact time/g-cat min g-PP^{-1}						
	20.0				26.2	34.7	82.5
	10 min[b)]	45	126	165	10 min	10 min	10 min
Hydrogen	3.2	2.6	2.2	2.1	5.1	4.4	5.6
Normal alkanes	9.8	7.8	6.4	6.2	11.7	16.1	20.9
Isoalkanes	32.0	19.4	13.4	11.9	32.2	38.2	47.2
Alkenes	48.4	67.3	76.1	77.4	46.5	35.8	19.9
Aromatics	6.6	2.9	2.0	1.7	4.5	5.0	6.5
H/C ratio of products	2.12	2.07	2.05	2.03	2.18	2.21	2.27
Molar ratio of aromatics to aliphatics (C_6-C_{12} fractions)	0.41				0.49	0.47	0.84

a) Composition: mol%, reaction temperature: 477 °C. b) Reaction time.

similar result is probably available over CaX.

Since polypropylene is presumably decomposed thermally to some extent under conditions of catalytic degradation, the characterization of the products in thermal degradation is of great significance to clarify the catalytic degradation mechanism. The product distribution in thermal degradation is shown in Table 4. The composition of the liquid fractions was very complicated consisting of about ninety components of C_5—C_{24} fractions. The identification of each component was further complicated because of many diastereomeric isomers derived from methyl branchings along the polymer chain. However, the chromatogram was simplified after hydrogenation, because three peaks of alkane, alkamonoene and alkadiene with the same carbon skeleton became a single peak of alkane. So, the liquid products were identified from the analysis of the hydrogenated products according to the method by Sugimura *et al.*[10)] Main products were propylene, 2-methyl-1-pentene (propylene dimer), 2,4-dimethyl-1-heptene (trimer), 2,4,6-trimethyl-1-nonenes (tetramers consisting of two diastereomeric isomers), and 2,4,6,8-tetramethyl-1-undecenes (pentamers of four diastereomeric isomers), the formations of which have been explained in terms of a radical mechanism involving intramolecular radical transfer to the tertiary carbon atoms in the secondary radicals and subsequent β-scission.[8)] This product distribution was approximately in line with the results by other investigators.[6—8)] The saturated hydrocarbons in the liquid fractions were pentane, 2-methylpentane, 4-methylheptane, and 4,6-dimethylnonanes (two diastereomeric isomers), but these hydrocarbons except for pentane were minor products. From the results obtained here, the thermal degradation of polypropylene is characterized as follows: The C–C bonds of the chain are preferentially broken and structual isomerization or demethylation of branchings hardly occurs. Most of the products are 1-alkenes. Monomethyl-branched hydrocarbons are limited to isobutylene, 2-methylpentane, 2-methyl-1-pentene and 4-methylheptane. The products of carbon number greater than 8 are branched hydrocarbons with two or more methyl branchings at the even-numbered carbons. Linear hydrocarbon except for C_1—C_3 fragments is pentane only.

As evident from the comparison between catalytic and thermal degradation products, the formation in a large quantity of aromatics and monomethyl-branched hydrocarbons, especially with branchings at the odd-numbered carbons, and higher degree of saturation of the products are remarkable in catalytic degradations. From these characteristics, the catalytic degradation of polypropylene can be considered to proceed to a large extent through aromatization, isomerization and hydrogen transfer reactions together with the C–C bond scission of the chain, and the tertiary carbonium ions which are readily formed because of methyl branchings along the polymer chain would be predominant intermediates.[4)] If isomerization or aromatization hardly occurs, the hydrocarbons produced by β-scission of the tertiary carbonium ions should be the same types as those by β-scission of the tertiary radicals in thermal degradation, and further if no hydrogen transfer reaction occurs, most of the products should be alkenes. However, the difference in product distribution of catalytic and thermal degradations would indicate that such fragments listed in Table 4 as main components further isomerize, cyclize or are saturated in catalytic degradation, resulting in the formation of aromatics and monomethyl alkanes. At the present stage of this study, however, a detailed mechanism is not clear.

The effects of contact time and reaction time on the composition of the products obtained over silica-alumina are shown in Table 5. A longer contact time promoted further degradations of liquid fractions to give the increase in the relative yield of gaseous products. The further degradations would be attributed to those of aliphatic hydrocarbons, and aromatics would hardly undergo further degradation, because the amount of aromatics and their composition changed very little with contact time. This low reactivity of aromatics with methyl groups is readily expected from their great stability. Therefore, the increase in the ratio of aromatics to aliphatics in C_6—C_{12} fractions with contact time is a reasonable result.

The product composition was also dependent on reaction time. More alkenes were produced (Table 5) and the distribution of the products shifted to higher carbon numbers (Table 1) as increasing reaction time, *i.e.*, progressing deactivation of silica-alumina catalyst. Even after 3 h, however, the products were concentrated on smaller carbon numbers compared to those obtained by thermal degradation. Similar results were obtained over CaX, but the catalyst deactivated with reaction time more rapidly than silica-alumina, as can be seen from the larger shift in product distribution shown in Table 1. Over both catalysts, high-boiling-point products were formed in increasing amount as reaction time lengthened, but the fractions of carbon number from 16 to 24 were absent in significant amounts. The gas chromatographic conditions used in the present study were enough to detect quantitatively the fractions of carbon number up to about 24. Therefore, the high-boiling-point products were estimated to be hydrocarbons with carbon number of at least greater than 24. Further, high viscous products showing wax-like aspect at room temperature were obtained when CaX catalyst was largely deactivated, suggesting the presence of such hydrocarbons with high molecular weight as estimated above. Although there is no evidence in the results obtained here for determining whether the degradation of polypropylene in the presence of the catalysts is initiated catalytically or thermally, the thermal initiation reaction would undoubtedly occur at reaction temperature of 477 °C and the catalytic initiation is also likely to occur. Kodaira *et al.*[4] showed by thermogravimetric analysis that polypropylene was decomposed at lower temperature by 50—100 °C in the presence of natural zeolite than that in the absence of the catalyst. This would suggest the participation of the zeolite catalyst in the initiation reaction and probably the catalytic initiation reaction takes place at external surface or neighborhood of pore mouth of the catalyst. In this study, therefore, it seems reasonable to assume that polypropylene is first decomposed thermally or catalytically to produce fragments of various sizes and then smaller fragments, which are able to diffuse into pores of the catalysts, selectively proceed to catalytic degradation, whereas larger fragments which can not diffuse into catalyst pores turn out as high-boiling-point products.

As described above, contact time and reaction time had large effects on alkene content, which was expected to be closely associated with coke deposition, and so the amount of coke deposited on catalyst was determined in each series of experiments by measuring the increase in catalyst weight. As is known commonly in catalytic cracking reaction, the relation between the weight percent of coke on catalyst, C, and reaction time, t,[17] is given as follows:

$$C = at^n,$$

where a and n are constant. The results of the present experiments using silica-alumina and CaX catalysts are shown in Fig. 2. The deposition of coke on silica-alumina followed the above relation. On the other hand, the relation in the case of CaX was satisfied only during the first 50 min on stream and after about 100 min the coke formation was substantially stopped. Figure 3 shows the dependence of the rate of coke formation on reaction time. Coke formation was extremely rapid in the initial reaction stages, at which CaX had nearly twice the rate of coke formation compared with silica-alumina, but the rate showed a severe decline with reaction time, while the decline was much less severe on silica-alumina. The amount of coke deposited during 3 h was nearly independent of feed rate over both catalysts. This observation means that the weight percent of coke on feed increases with contact time, that is, coke is more susceptible to deposition under a condition of longer contact time to produce less amount of alkenes.

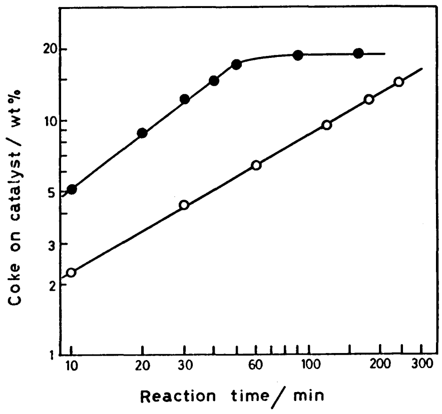

Fig. 2. Relation between coke deposition and reaction time at 477 °C.

○: Silica-alumina at F=0.116 g-PP min^{-1}, ●: CaX at F=0.122 g-PP min^{-1}.

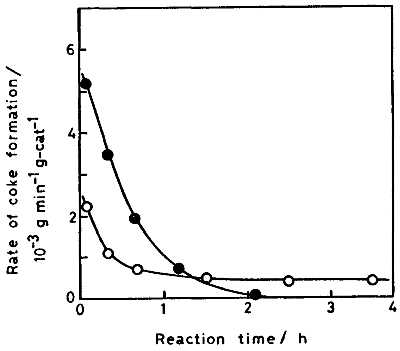

Fig. 3. Variation in rate of coke formation with reaction time.

Reaction conditions: See Fig. 2. ○: Silica-alumina, ●: CaX.

In this study, it was possible to evaluate the H/C ratio of the products. As the H/C ratio of polypropylene, $(C_3H_6)_n$, is 2, it should be also 2 for total degradation products provided that coke deposition is negligibly small. The ratio, in fact, was 2.03 in the thermal degradation. A slight deviation from the theoretical value of 2 would be due to the assumption that all of alkenes and high-boiling-point products were alkamonoenes. If some alkadienes are contained in

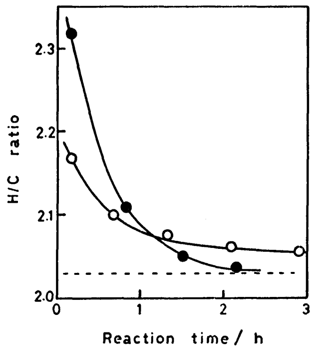

Fig. 4. Dependence of H/C ratio of products on reaction time.
Reaction conditions: See Fig. 2. ○: Silica-alumina, ●: CaX. ----: Level in thermal degradation under the same conditions as Table 4.

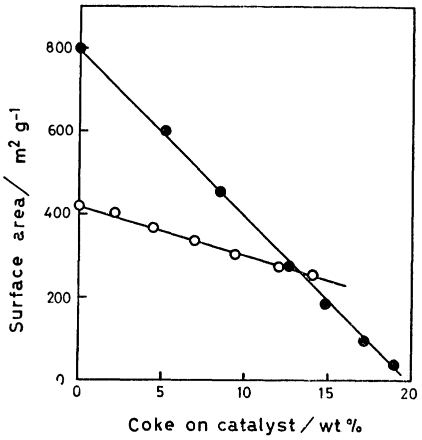

Fig. 5. Effect of coke on surface area of catalyst.
Reaction conditions: See Fig. 2. ○: Silica-alumina, ●: CaX.

the thermal degradation products, and this can probably be so, the ratio approaches 2. On the other hand, the H/C ratios of catalytic degradation products were greater than 2 and reduced with reaction time as shown in Fig.4. The curves in the figure resembled those of the rate of coke deposition (Fig. 3) in shape. When the rate over CaX became nearly zero in about 2 h, the ratio reached to the level of the products by thermal degradation. Therefore, the reduction of the H/C ratio with increasing reaction time is concluded to result from the decrease in coke deposition since the supply of hydrogen from a coke precursor to unsaturated molecules, *i.e.*, hydrogen transfer, leads the H/C ratio greater than 2. The hydrogen transfer occurs also in aromatization process, but it has no effect on the ratio. Thus, the H/C ratio of products will be a good and qualitative indicator for expressing the degree of formation of coke. By taking into account the coke deposition, the effects of contact time and reaction time on alkene content were reasonably explained. As aromatics are much more strongly adsorbed on acid catalysts than more saturated hydrocarbons, it seems reasonable to assume that aromatics, particularly of condensed rings such as naphthalenes, most closely relate to coke deposition.[18,19]

Figure 5 shows that the accumulation of coke exerts its effect by reducing surface area of the catalysts. About 95% loss in surface area was observed at 19 wt% of coke on CaX catalyst. This level of coke deposition would be close to a limiting degree in the reaction conditions. More pronounced reduction in surface area of CaX compared with silica-alumina makes possible to assume that CaX catalyst with smaller pores is susceptible to clogging of its pore structure by coke and consequent elimination of accessible surface. As the clogging disturbs the diffusion of reactants or products, coke itself is a diffusion barrier. This pore clogging may occur more or less on silica-alumina, but apparently it does not occur to the same extent as on CaX. The coke deposition, of course, is dependent on acidic properties of catalyst, but depends also on pore structure. Therefore, it seems clear that the formation of coke has large effect on catalyst diffusivity.

References

1) K. Murata and T. Makino, *Nippon Kagaku Kaishi*, **1975**, 192.

2) H. Nishizaki, M. Sakakibara, K. Yoshida, and K. Endoh, *Nippon Kagaku Kaishi*, **1977**, 1899.

3) Y. Uemichi, A. Ayame, and H. Kanoh, *Nippon Kagaku Kaishi*, **1980**, 1741.

4) I. Kodaira, Z. Osawa, and H. Ando, *Nippon Kagaku Kaishi*, **1977**, 1892.

5) T. Yamaguchi, T. Kamiguchi, T. Ito, S. Ohkita, and T. Goto, *Nippon Kagaku Kaishi*, **1976**, 1171.

6) T. A. Iida, T. Iida, H. Nozaki, and M. Sukigara, *Nippon Kagaku Kaishi*, **1976**, 837.

7) Y. Tsuchiya and K. Sumi, *J. Polym. Sci., Part A-1*, **7**, 1599 (1969).

8) E. Kiran and J. K. Gillham, *J. Appl. Polym. Sci.*, **20**, 2045 (1976).

9) M. Seeger and H. J. Cantow, *Makromol. Chem.*, **176**, 2059 (1975).

10) Y. Sugimura, T. Nagaya, S. Tsuge, T. Murata, and T. Takeda, *Macromolecules*, **13**, 928 (1980).

11) Y. Uemichi, A. Ayame, Y. Kashiwaya, and H. Kanoh, *J. Chromatogr.*, **259**, 69 (1983).

12) F. D. Rossini, E. J. Prosen, and K. S. Pitzer, *J. Res. Nat. Bur. Stand.*, **27**, 529 (1941).

13) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **36**, 559 (1946).

14) S. H. Hastings and D. E. Nicholson, *J. Chem. Eng. Data*, **6**, 1 (1961).

15) H. H. Voge, G. M. Good, and B. S. Greensfelder, *Ind. Eng. Chem.*, **38**, 1033 (1946).

16) M. Nakamura, *J. Jpn. Petrol. Inst.*, **16**, 51 (1973).

17) A. Voorhies, Jr., *Ind. Eng. Chem.*, **37**, 318 (1945).

18) W. G. Appleby, J. W. Gibson, and G. M. Good, *Ind. Eng. Chem., Process Des. Dev.*, **1**, 102 (1962).

19) P. E. Eberly, Jr., C. N. Kimberlin, Jr., W. H. Miller, and H. V. Drushel, *Ind. Eng. Chem., Process Des. Dev.*, **5**, 193 (1966).