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Transformation of Butanes over ZSM-5 Zeolites

Part 1.—Mechanism of Cracking of Butanes over H-ZSM-5

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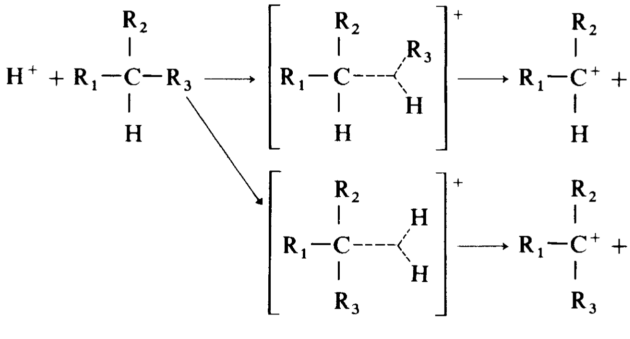
The transformations of butane and isobutane over H-ZSM-5 have been studied at 773 K with a special emphasis on the mode of activation of butanes on the acidic sites. The change in the product selectivity with the total conversion of butane (and isobutane) was examined. At low conversion levels, butane is cracked exclusively by a carbonium-ion mechanism into three combinations of products, $CH_4 + C_3H_6$, $C_2H_6 + C_2H_4$, and $H_2 + C_4H_8$. The contributions of the three pathways are 42–44%, 38–36% and 20%, respectively. The ratio does not depend on the partial pressure of butane. As the degree of conversion increases, the formation of propane increases, indicating that the activation of butane by a hydride-transfer mechanism is involved. Thus, in the conversion range 20–40%, the contribution of the carbonium-ion mechanism is reduced to 50–60%, 40–50% of butane being activated by the hydride-transfer mechanism. The contribution of the hydride-transfer mechanism increases as the partial pressure of the reactant increases.

At very low conversion levels, isobutane undergoes cracking through a carbonium-ion mechanism to form $(CH_4 + C_3H_6)$ and $(H_2 + C_4H_8)$ with a ratio of 2 : 1. At higher conversion levels the activation by the hydride-transfer mechanism predominates. In the conversion range 13–24% this mechanism accounts for *ca*. 60% of isobutane activation.

Whilst the cracking of alkanes has been a subject of continued interest for many years, the mechanism of cracking still remains controversial. For a long time, a hydride-transfer mechanism

$$R_1H + R_2^+ \rightarrow R_1^+ + R_2H \qquad (1)$$

was considered to be the main mechanism for alkane activation.[1,2] In 1984, Haag and Dessau[3] stressed the importance of the mechanism involving a pentacoordinated carbonium ion as follows


(2)

This mechanism had been adapted from that proposed for the cracking of alkanes in superacid media.[4]

Abbot and Wojciechowski[5] studied the cracking of C_6–C_{16} alkanes over HY zeolite, and concluded that the cracking reactions are initiated by direct C—C bond cleavage through mechanism (2) for linear alkanes. They concluded that C—H bond cleavage is also involved for short branched alkanes but that hydride transfer is more important than protolysis in the overall reaction. Lombardo and Hall[6] found that, in the cracking of neopentane over a variety of solid acids, *ca.* one methane molecule was formed for every neopentane reacted and concluded that the protonation of a C—C bond of neopentane is the preferred pathway in cracking this alkane. They also studied the cracking of isobutane over SiO_2–Al_2O_3, HZSM-5, HY and H-mordenite. They demonstrated that, over all these catalysts, two primary reactions occur, resulting in the formation of methane and hydrogen and concomitantly butyl and isopropyl cations, and that hydrogen-transfer is more important in the conversion of isobutane than neopentane.[7]

This work is concerned with the mechanism of cracking of butane and isobutane over H-ZSM-5 at 773 K. Research on alkane cracking has been confined to larger molecules such as decane because of their practical importance. However, it is important to extend our basic knowledge on the cracking mechanism to the activation of smaller molecules such as butanes in order to discover the routes for the transformation of smaller alkanes into more valuable chemicals such as aromatics.

The results obtained in this work should give useful information for discussing the transformation of butanes into aromatic hydrocarbons over Zn-ZSM-5 and Ga-ZSM-5 at the same temperature, which will be described in the following paper.[8]

Experimental

ZSM-5 zeolite ($SiO_2/Al_2O_3 = 56$) was synthesized by a patented method.[9] The structure of the synthesized material was confirmed to be that of ZSM-5 by X-ray diffraction. The synthesized material was converted into the ammonium form (NH_4-ZSM-5) by using the procedure described by Jacobs.[10] The NH_4-ZSM-5 was pressed, crushed and sorted into grains of 16–32 mesh. The reactions were carried out in a continuous-flow reactor at atmospheric pressure. The NH_4-ZSM-5 was packed into a reactor of silica-tubing (10 mm i.d.), placed in a vertical furnace and then heated under an air stream at 823 K for 90 min. By this treatment NH_4-ZSM-5 was expected to be converted into the proton form (H-ZSM-5). Butane, isobutane and nitrogen were fed into the reactor through flow meters. The effluent gas was withdrawn periodically and analysed by gas chromatography.

Results and Discussion

Butane Cracking

The dependence of the total conversion and the product selectivity on contact time in butane cracking over H-ZSM-5

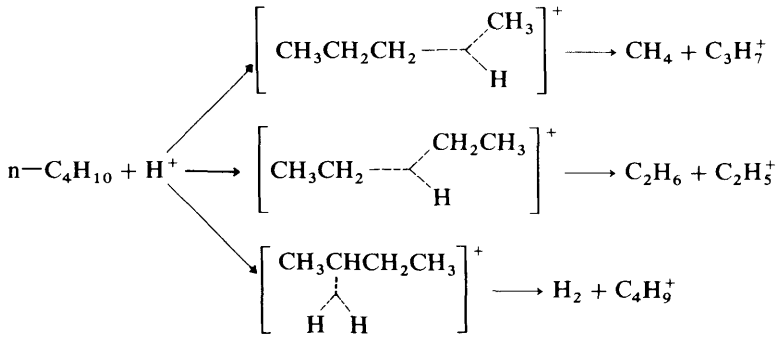
Table 1 Dependence of product selectivity on contact time in butane cracking (8.0 kPa) at 773 K

(*W*/*F*) /g h mol^{-1}	conversion (%)	selectivity/mol in 100 mol butane converted											
		CH_4	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$	C_5H_{12}	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_{6+}	aromatics	H_2
0.075	0.57	49	39	2.4	2.3	0	36	37	18	0	0	0	28
0.085	0.71	40	36	2.3	2.4	0	33	33	27	0	0	0	—
0.1	1.82	42	36	2.6	1.6	0	34	33	26	0	0	0	—
0.2	1.61	42	39	4.8	1.5	0	38	34	21	0	0	0	—
0.4	3.7	33	33	8.6	1.4	0	35	31	27	0	0	0	21
0.6	5.4	32	32	13	1.7	0	37	30	24	0	0	0	20
0.8	7.3	31	31	16	1.5	0	37	29	22	0	0	0.3	21
1.0	9.2	29	30	18	1.7	0	37	30	21	0	0	0.3	20
2.0	19.2	32	29	22	1.8	0	38	29	16	0	0	0.7	19
3.0	29.1	27	28	29	2.3	0	38	30	12	0	0	1.8	21
4.2	39.1	26	27	33	2.6	0	35	27	11	0.4	0	2.9	17
—	0[a]	42	38	0	0	0	33	34	27	0	0	0	20

[a] Extrapolated.

was examined at partial pressures of butane of 8.0 and 34.2 kPa at 773 K. Table 1 shows the results of the reactions of butane at partial pressure of 8.0 and 34.2 kPa, respectively. Here, contact time is expressed as *W*/*F*, where *W* and *F* are the weight of catalyst (g) and the total feed rate of (butane + nitrogen) in mol h^{-1}. The selectivities are expressed as the number of moles of each product formed per 100 moles of butane converted.

It is obvious from Table 1 that, in the conversion at the lower pressure, the main products at low conversion levels are methane, ethane, ethene, propene, butenes and hydrogen. As the conversion increases, propane becomes one of the major products. In Fig. 1, the selectivities are shown as a function of the total conversion of butane. By extrapolating the selectivity *vs.* conversion curves to zero conversion, the selectivities in the primary reactions are obtained. The extrapolated values are also listed in Table 1. This again shows more clearly that the six species mentioned above are the real primary products. Thus, the primary reactions at low conversion levels are explained by mechanism (2), namely, the activation of butane *via* carbonium-ion intermediates.



(3)

(4)

(5)

The carbenium ions, $C_3H_7^+$, $C_2H_5^+$ and $C_4H_9^+$, may release a proton and then propene, ethene and butenes are formed, respectively. The numbers of moles of the two products which are expected from each of reactions (3)–(5), *e.g.* those of methane and propene, do not completely coincide, indicating that the alkenes (or carbenium ions) undergo secondary reactions before they leave the pore system of the zeolite. At any rate, reactions (3)–(5) explain the preponderance of the six products and this infers that only mechanism (2) prevails at the first stage of the cracking.

The ratio of the contribution of the three reactions (3)–(5) can be estimated from the selectivity ratio of methane, ethane and hydrogen. The extrapolated selectivities show that the three reactions occur with a ratio of 42 : 38 : 20, the cleavage of the C—C bonds being more prevalent than the cleavage of the C—H bonds. This agrees with the results obtained in cracking reactions in superacid media.[4]

In the later stages, the selectivities for methane, ethane and hydrogen decrease as shown in Fig. 1. If reactions (3)–(5) were the only route for butane activation, the selectivities for these inert products should be constant at any conversion level, although the selectivities for more reactive intermediates could change substantially because of the secondary reactions. This means that another way of activating butane, namely mechanism (1), becomes important at higher conversion levels. This is reflected by the high yields of propane in the later stages. Propane is plausibly formed by the reaction

$$n\text{-}C_4H_{10} + C_3H_7^+ \rightarrow C_3H_8 + C_4H_9^+ \qquad (6)$$

The dimethylcarbenium ion, $(CH_3)_2CH^+$, may be the predominant active species, and is produced through alkene dimerization, isomerization and cracking. Thus, if the activation of butane occurs by eqn. (6), methane, ethane and hydrogen are not produced and, accordingly, the selectivities for these products decrease. The selectivities for methane, ethane and hydrogen at 39.1% conversion are 26, 27 and 17 mol per 100 mol of butane converted. This means that on average 70% of reacted butane molecules are activated *via* pentacoordinated carbonium ions.

The mechanism that prevails in the later stages can be more accurately estimated by calculating the increment of each product between two conversion levels. Thus, calculation revealed that the average selectivities between the total butane conversion of 19.2 and 39.1%, are 20, 24 and 15 for methane, ethane and hydrogen, respectively. This means that between these two conversion levels, *ca.* 60% of butane mol-

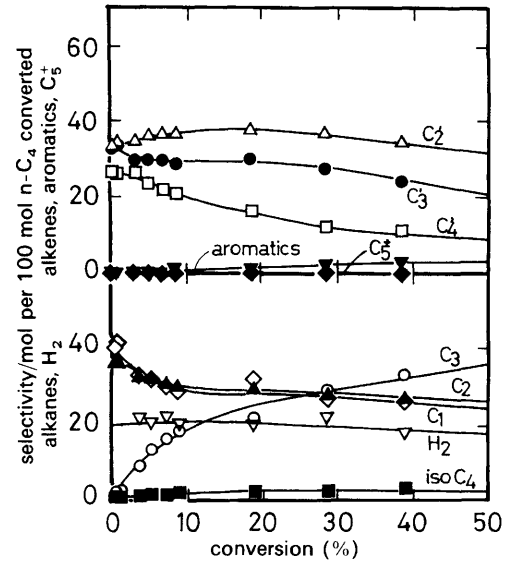


Fig. 1 Product selectivity as a function of conversion of butane over H-ZSM-5. Reaction temperature, 773 K; butane pressure, 8 kPa

ecules are activated *via* mechanism (2) and the other 40% *via* mechanism (1). Since methane and ethane could also be formed by secondary reactions, the actual contribution of mechanism (2) could be lower than 60%.

There must be equilibria between alkenes and protons (or acidic OH groups) on the surface of the zeolite:

$$R_1R_2C{=}CR_3R_4 + H^+ \rightleftharpoons R_1R_2CH{-}\overset{+}{C}R_3R_4; \quad R_i = \text{alkyl or H} \quad (7)$$

Therefore, once alkenes are formed, the equilibria shift to the right-hand side, and this increases the concentration of carbenium ions and decreases that of protons. This may explain the shift of the mechanism of the mode of activation of butane with increasing total conversion.

A similar argument can be followed for the cracking of butane at a partial pressure of 34.2 kPa. The selectivity *vs.* conversion curve for this case is shown in Fig. 2. The general trend of the course of the reaction is similar to that in the cracking of butane with a partial pressure of 8.0 kPa and the main products are the same. From the selectivities to methane, ethane and hydrogen, the ratio of the contributions of reactions (3)–(5) is estimated as 44 : 35 : 21. Note that this ratio is very close to that obtained in the cracking of butane at 8.0 kPa (42 : 38 : 20). Therefore, the mode of activation of butane does not depend on the partial pressure of butane at the very beginning of the reaction, and the activation occurs exclusively through mechanism (2).

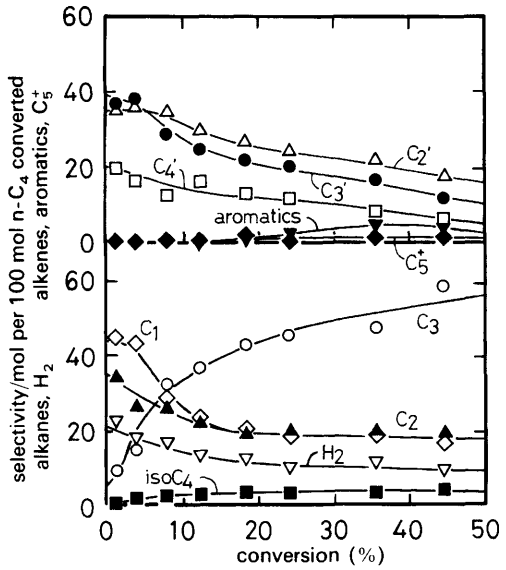


Fig. 2 Product selectivity as a function of conversion of butane over H-ZSM-5. Reaction temperature, 773 K; butane pressure, 34.2 kPa

The effect of pressure is, however, observed in the later stages. As shown in Fig. 2, the decrease in selectivities to the initial six products is more significant at higher pressure and the propane yield increases more sharply with increasing total conversion. Thus, when the total conversion of butane was 44.7%, the selectivities for methane, ethane and hydrogen were 17, 20 and 11 mol per 100 mol of butane converted, respectively. The contribution of mechanism (2) for butane activation is thus *ca.* 50%.

If we calculate the average selectivities between the two conversion levels of 18.7 and 43.3%, the selectivities for methane, ethane and hydrogen are 9, 15 and 19%, respectively. Thus, the contribution of mechanism (2) in this conversion range accounts for only 43% of the butane molecules reacted. The remainder (57%) must be activated by mechanism (1). In contrast to the cracking of butane at 8.0 kPa, the participation of mechanism (1) now predominates over mechanism (2). This result is expected if one considers the equilibria of eqn. (7). At higher pressure, a higher concentration of alkenes is attained in the zeolite pores to shift the equilibria to the right-hand side. The higher concentration of carbenium ions and lower concentration of protons should favour mechanism (1) over mechanism (2). This is reflected in a higher yield of propane at higher pressures.

The effect of pressure on the selectivity in butane cracking was examined at 773 K in more detail. Fig. 3 shows the dependence of the total conversion of butane on its partial pressure. The total conversion increases slightly with butane pressure, indicating that the order of the reaction is slightly higher than unity. In Fig. 4, the selectivity for each product was plotted as a function of the partial pressure. Although the total conversion does not change significantly (Fig. 3), the selectivity in the cracking changes drastically with the partial pressure. The selectivities for methane, ethane, hydrogen and lower alkenes decrease with partial pressure, while those for propane and isobutane increase. This again shows that the mode of activation of butane changes with the partial pressure. From the selectivities for methane, ethane and hydro-

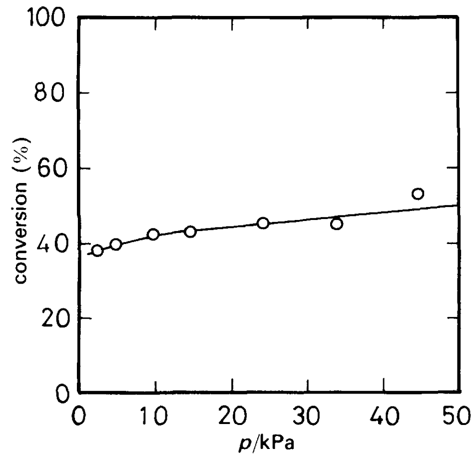


Fig. 3 Effect of the partial pressure of butane on the total conversion over H-ZSM-5. Reaction temperature, 773 K; $W/F = 4.2$ g h mol^{-1}

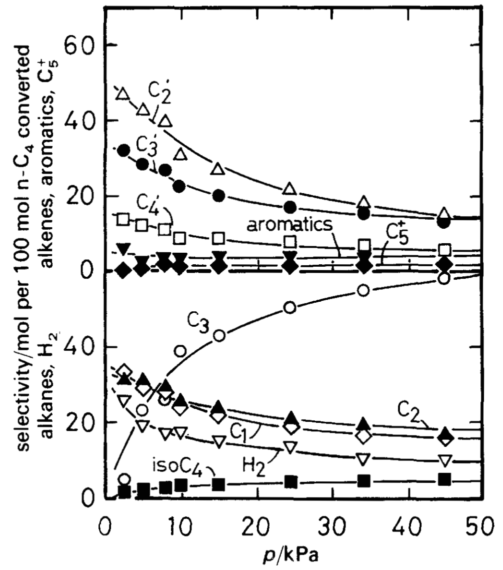


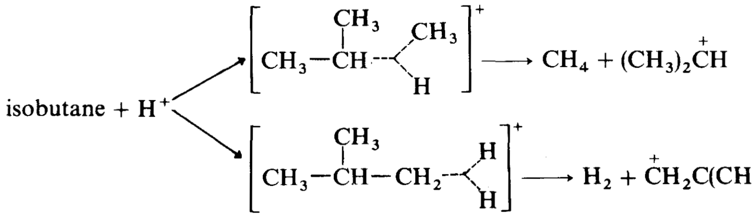
Fig. 4 Effect of the partial pressure of butane on the product selectivity in butane conversion over H-ZSM-5. Reaction temperature, 773 K; $W/F = 4.2$ g h mol^{-1}

gen, the contribution of mechanism (2) was estimated. At 2.5 kPa, the contribution of mechanism (2) amounts to 92% at conversion levels as high as 38%; at 45 kPa, the contribution decreases to 46%.

Isobutane Cracking

Fig. 5 shows the dependence of the product selectivity in isobutane cracking on the total conversion at 773 K. The reaction was carried out by feeding 8.0 kPa of isobutane together with nitrogen. The primary products at low conversion levels are methane, propene, hydrogen and butenes. In the later stages, ethene and propane are formed in significant amounts.

The initial products suggest that the activation of isobutane occurs *via* a carbonium-ion mechanism, namely, the following two reactions.



$$\text{isobutane} + H^+ \rightarrow \left[CH_3-\overset{CH_3}{\overset{|}{CH}}\cdots\left\langle{}^{CH_3}_{H}\right.\right]^+ \longrightarrow CH_4 + (CH_3)_2\overset{+}{C}H \qquad (8)$$

$$\text{isobutane} + H^+ \rightarrow \left[CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2\cdots\left\langle{}^{H}_{H}\right.\right]^+ \longrightarrow H_2 + \overset{+}{C}H_2C(CH_3)_2 \qquad (9)$$

The selectivities for methane and hydrogen at zero conversion, estimated by extrapolation, reveal that reactions (8) and (9) occur with a ratio of 67 : 33. The selectivities for propene and butenes also give similar values, showing that reactions (8) and (9) constitute the mechanism operating at low conversion levels, in agreement with the results obtained by Lombardo and Hall.[6,7]

In the later stages, the selectivities for the four products decline and those for ethene and propane increase. The decrease in the selectivities for methane and hydrogen suggest that the mechanism of isobutane activation changes with the conversion level. At the total conversion of 23.6%, the selectivities for methane and hydrogen are 39 and 30 mol per 100 mol of butane converted, respectively. Thus, a drastic decline of the C—C bond cleavage is obvious. Overall, mechanism (2) accounts for 69% of isobutane activation.

The calculation of the average contribution of mechanism (1) between the two conversion levels, 13.4 and 23.6%, shows that only 40% of isobutane is activated by mechanism (2) and that the remainder must be activated by mechanism (1).

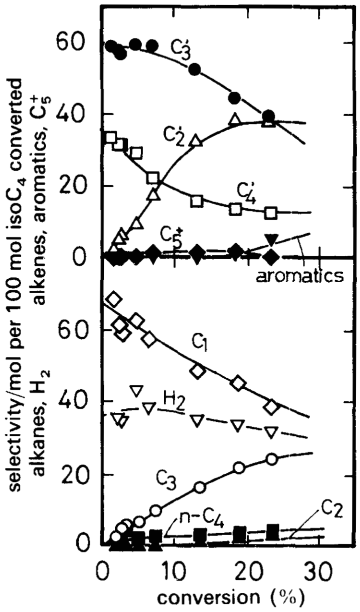


Fig. 5 Product selectivity as a function of conversion of isobutane over H-ZSM-5. Reaction temperature, 773 K; isobutane pressure, 8.0 kPa

The increase in selectivity for ethene shows that interconversion between alkenes is very fast. Formation of propane is brought about by hydrogen transfer between a dimethylcarbenium ion and an isobutane molecule.

Fig. 6 shows the selectivity for the reaction as a function of the partial pressure of isobutane. In this pressure range the conversion of isobutane is almost independent of the pressure (*ca.* 25%), the cracking being first order with respect to the reactant.

Even though the kinetics are simple, the product distribution depends very much on the partial pressure. The decrease in selectivities for methane and hydrogen at higher pressures is obvious. The selectivities for the two products were 42 and 35% at 3.0 kPa, while they were 28 and 25% respectively at 46 kPa. Thus, the contribution of mechanism (2) decreases from 77 to 53% when the partial pressure increases from 3.0 to 46.2 kPa.

Thus, as in the case of butane cracking, the contribution of mechanism (2) increases with the partial pressure of isobutane. This is reflected in the higher selectivity for propane at higher isobutane pressure.

Conclusions

At very low conversion levels, the activation of butanes occurs almost exclusively *via* a carbonium-ion mechanism, irrespective of the pressure of butanes.

As the conversion levels increase and alkenes are accumulated in the system, a hydride-transfer mechanism becomes

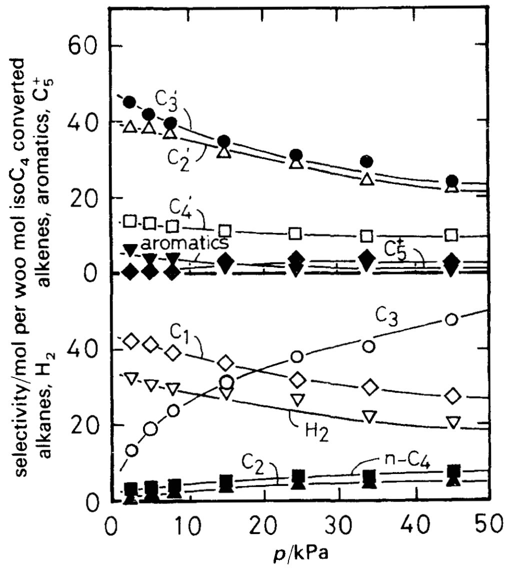


Fig. 6 Effect of the partial pressure of isobutane on the selectivity in isobutane conversion over H-ZSM-5. Reaction temperature, 773 K; $W/F = 4.2$ g h mol^{-1}

operative. Its contribution increases with increasing conversion level.

The contribution of hydride transfer in the later stages is more significant at a higher partial pressure of butanes.

The product distribution is greatly affected by the partial pressure of the reactant, even when the cracking apparently obeys first-order kinetics.

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