CHAPTER 2. LITERATURE SURVEY - N-BUTENE SKELETAL ISOMERISATION

2.1 INTRODUCTION

Before embarking on a detailed investigation of the skeletal isomerisation of the n-butenes to isobutene, the suitability of existing commercial processes should be evaluated. If the alternatives available are not suitable for implementation at Sasol, then a detailed study of the direct skeletal isomerisation of the n-butenes to isobutene will be justified. This should involve a review of the relevant literature pertaining to the skeletal isomerisation of the n-butenes to isobutene, with an emphasis on the nature of the side reactions, the thermodynamic limitations of the process, the reactivity of the products in subsequent processes, specifically etherification, the kinetics and mechanisms of the reactions, the catalysts used by other workers and the properties of the material under study. The review of the literature will be restricted to amorphous catalyst, as the material studied was of this type. A detailed description of the experimental, analytical and mathematical procedures used during this study are given in Chapter 3 and Appendices 1 and 2. The results from a detailed investigation as to the effects of the operating conditions are discussed in Chapter 4. In Chapter 5 and Chapter 6, as well as in Appendix 3 to 5, the details of the experimental and computational procedures used while attempting to identify the n-butene skeletal isomerisation mechanism are given. The overall conclusions and recommendations are presented in Chapter 7 followed by the references.

2.2 ALTERNATIVE SOURCES OF ISOBUTENE

Isobutene has many uses, some of which are shown in Figure 2.1 below, and may be obtained from a variety of sources. A brief description of some of these is presented below. A limited quantity of isobutene occurs in natural gas, associated with crude oil production, and in reservoir gas. However, the main sources of isobutene within the gates of the crude oil refineries are the steam and catalytic crackers. The C4 cuts from these units, approximately 15 % of the total product, can contain as much as 45 mass % and 15 mass % isobutene respectively.

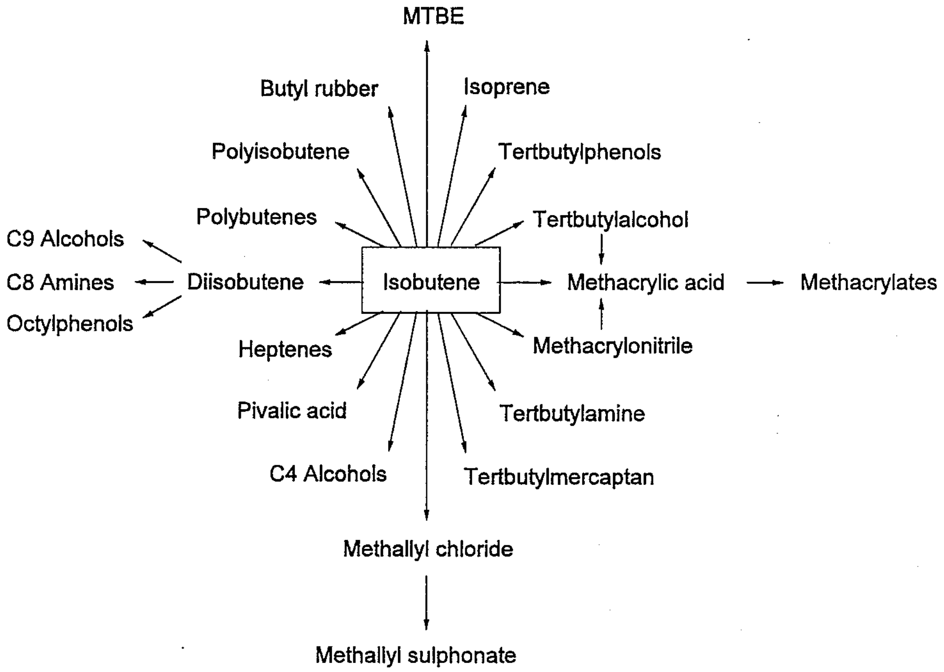


Figure 2.1 : Isobutene end uses in the production of chemicals (Fattore et al., 1981:101)

However, the demand for gasoline additives, i.e., tertiary ethers, can not be met by using the isobutene available in these streams (Muddarris and Pettman, 1980:92).

Butenes can also be produced via the dehydrogenation of the butanes to the corresponding butenes using a number of commercially proven catalytic processes. An example of this technology is the Houdry Catofin Process, which is an adiabatic fixed bed multi-reactor catalytic procedure. In this process the operating conditions are so chosen that the heat required for the endothermic dehydrogenation reaction is substantially equal to the exothermic heat of combustion of the coke deposited during the on line period. Short on-line times of between 5 to 10 minutes are used during which approximately 0.5 mass % coke is deposited. The reactors are run at a temperature of between 550°C to 650°C and a pressure of 0.15 to 1 bar(a) using a chromic oxide catalyst. To ensure continuous operation of the process, a minimum of three reactors are required, with one reactor on stream, a second being regenerated and the third completing either a purging or valve changing step (Logwinuk and Craig, 1964:66).

To increase the yield of isobutene from the dehydrogenation step, the unit may be preceded by a paraffin hydro-isomerisation unit. Suitable paraffin isomerisation processes might be the UOP (Schmidt et al., 1989:1) or the BP process (Burbidge, 1980:169). In the BP process high purity isobutane is prepared in the presence of hydrogen over a platinum containing catalyst. Operating the reactor at a pressure of between 13.6 bar to 27 bar, a temperature of 150°C to 200°C and a hydrogen to feed mole ratio of 0.1 to 5, near equilibrium conversion are achieved. The catalyst lifetime is in excess of 2 years with full recovery in activity after regeneration. A process of this nature is currently being used by the Saudi European Petrochemical Co to produce 12500 b/d of MTBE. Further details of a combined paraffin isomerisation and dehydrogenation flow sheet may be found in Vors et al. (1988:1).

An alternative to the dehydrogenation process is the KTI buta-cracking technology. This is a process in which isobutane can be cracked selectively to isobutene and propene. Indications are that the process is complex as optimal control of the temperature and pressure profiles, steam dilution, residence time, gas velocity, heat flux, conversion rate and quench techniques are required to achieve efficient operation (Monfils and Barendregt, 1990:2). Yet another alternative route from isobutane to isobutene is via the Arco process (Remirez, 1987:21). In this process an organic hydroperoxide is used as an oxygen carrier to epoxidise propene. Suitable starting materials are ethyl benzene and isobutane. Using the latter tertiary butyl hydroperoxide is formed which, together with propene is passed over a metal catalyst to give propene oxide and tertiary butanol. The latter can easily be dehydrated to isobutene (Abraham and Pescott, 1992:51).

Using zeolite or Amberlyst 15, Bell and Haag (1986:2) found that methanol could be reacted with propene to give methyl isopropyl ether. Although not substantiated by means of an example they further claim that tertiary-butanol and ethene may also be used to give ethyl tertiary butyl ether. Alternatively, the linear olefin can be substituted with another alcohol. Using n-propanol and methanol Ueda et al. (1992:1558) found that iso butyl alcohol may be synthesized directly over a MgO catalyst. Operating at 300°C they successfully converted the feed alcohols to iso butyl alcohol recording a yield of approximately 41 mass %.

Alternatively, iso butyl alcohol may be produced followed by and dehydration to isobutene. Iso butyl alcohol may be produced directly from coal via gasification and further reaction of the CO and H_2 as briefly discussed by Reynolds et al. (1975:51). A more detailed study of this process was done by, among others, Keim and Falter (1989:59). Using the CO hydrogenation route they found that iso butyl alcohol and methanol could be produced at a ratio of 5:1 over a catalyst containing Zr, Mn and K, at 250 atm and 693K.

Alternative process for the direct synthesis of isobutene include the methanol cracking process (Sherwin, 1981:81), which also produces aromatics and paraffins, or the dimerisation of propene. In anticipation of a natural rubber shortage in the early 60's a process was sought for the production of a synthetic rubber monomer. One such procedure was developed by Goodyear and Scientific Design (Anhorn and Frech, 1961:44). Using a tri-alkylaluminium catalyst operated at a temperature of between 150°C and 250°C at a pressure of 200 bar, propene conversion levels of 60 to 95 mass % were achieved with a 2-methyl-1-pentene yield of about 95 %. As the primary reaction when cracking the propene dimmer is the rupture of the carbon - carbon bond beta to the double bond in 2 methyl-1-pentene, isobutene and ethene can be produced in this way.

From the above discussion it may be seen that a variety of commercial and laboratory processes exist for the manufacture of isobutene. However, the high costs associated with the erection of new plants, feed stock limitations as well as the fact that the final product is a petrol additive, i.e., a low value product, make the use of the alternative technologies unattractive to Sasol. A process which is not available commercially is the skeletal isomerisation of the n-butenes to isobutene. A number of companies such as UOP, Lyondell, Texas Olefins, Mobil/BP, IFP, Shell and Sasol have been examining the feasibility of this route. The results of the work conducted at Sasol using an amorphous silica alumina catalyst supplied by an external company are presented in this thesis.

2.3 CHARACTERISTICS OF THE BUTENES

2.3.1 PHYSICAL PROPERTIES OF THE BUTENES

The chemical data and physical properties of the four isomers of butene were summarized by Kirk and Othmer (1984:346) and more extensively over a range of 1 to 1000 atm and 260 K to 600 K, by Das and Kuloor (1967a-c, 1968:75).

2.3.2 REACTIVITY OF THE BUTENES

As the products from the skeletal isomerisation are intended for use in an etherification process, with the desired product being tertiary ether, the reactivity of the various isomers for electrophilic addition type reactions was examined. This will give an indication whether the mixture of the isomers can be used as feed for the etherification unit or if purification of the feed is first required. The effects of the inert materials such as paraffins on the etherification reaction, are not considered at this point.

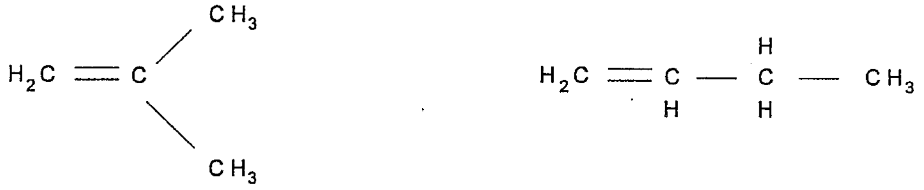
Examining the structure of the four butene isomers it was found that the substituent groups of the various isomers are quite differently arranged around the double bond, as shown schematically in Figure 2.2. It is therefore not surprising that the four isomers exhibit quite different electron densities, basicity, polarities and steric constraints or that the order of the reactivity of the butene isomers for electrophilic addition reactions, such as etherification, was reported by Fajula and Gault (1976:7691), to be :

isobutene >> 1-butene > *cis*-2-butene = *trans*-2-butene.

It is this difference in reactivity for electrophilic addition type reactions, such as etherification with methanol to form methyl tertiary butyl ether (MTBE), that allows the selective removal of isobutene from a mixture of the butene isomers. Primary or secondary ethers via the reaction of the linear butene with the alcohol, are not formed.

trans-2-butene

cis-2-butene



isobutene

1-butene

Figure 2.2 : Structure of the butene isomers (Ullman, 1985:483)

Hence, separating the isobutene from the linear butenes is not required to ensure a high yield of the desired tertiary ether during the subsequent etherification step. Furthermore, as the bond and skeletal isomerisation reactions are considered reversible, a high yield of the desired ether may be achieved by recycling the linear butenes to the isomerisation reactor. This of course requires that during the skeletal isomerisation reaction, the formation of by-products other than the linear butenes must be minimised.

2.3.3 REACTIONS OF THE BUTENES

The skeletal isomerisation of the n-butenes to isobutene may be achieved at atmospheric pressure and temperatures ranging from 300°C to 550°C with a variety of acidic catalysts. However, the selectivity to isobutene is restricted not only by thermodynamic constraints but also due to accompanying side reactions, which produce both low and high boiling components. More specifically, at the conditions commonly employed, 1-butene not only undergoes reversible bond isomerisation, i.e., the formation of *cis*-2- and *trans*-2-butene as well as skeletal isomerisation to isobutene, but also oligomerisation, cracking and hydrogenation. Of course, the extent to which these side reactions proceed can be controlled by the choice of a suitable catalyst and operating conditions (Condon, 1958:98). The overall scheme, summarizing the possible reactions of the butenes, is summarised in Figure 2.3.

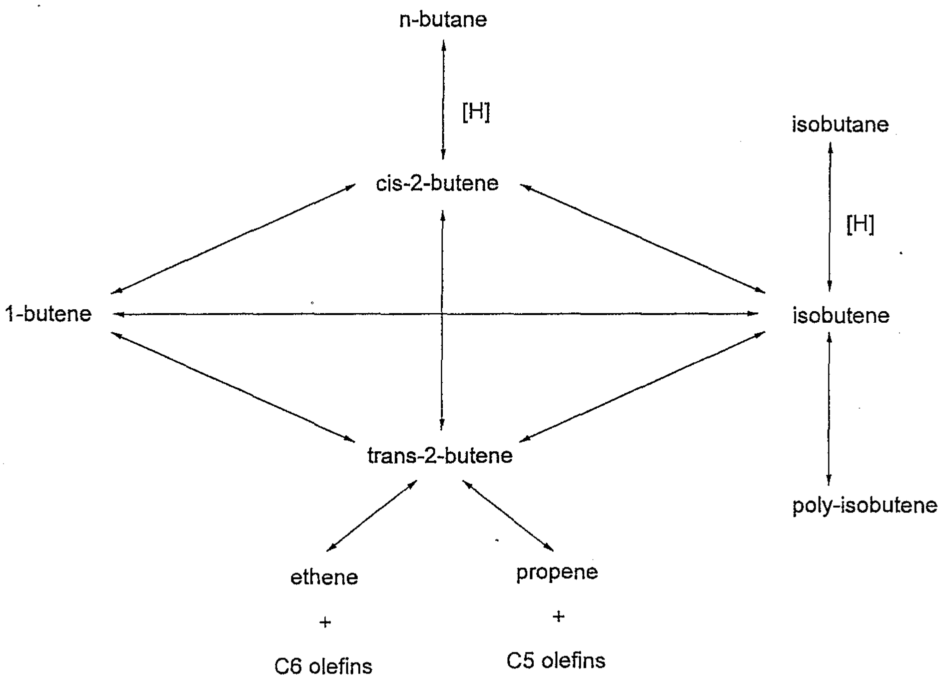


Figure 2.3 : Reactions of the butenes (Kirk and Othmer,1984:356)

Examining the various reaction in more detail it was found that this reaction scheme can be simplified. Double bond isomerisation of the butenes, as opposed to skeletal isomerisation, can be achieved at room temperature over acidic catalyst (Condon, 1958:99) or thermally at temperatures between 345°C and 420°C, without the formation of by-products. This, together with the results reported by Bianchi et al., (1994:556), who found that the bond isomerisation kinetics could best be represented by a first order reactions, with identical rate constants, suggests that the linear butenes may be treated a single pseudo-component, n-butene during the skeletal isomerisation reaction. The overall scheme as drawn by Ochoa and Santos (1995:286), is shown in Figure 2.4.

Considering the linear butenes as a pseudo-homogeneous species is in fact the most common approach used, as done by Bianchi et al. (1994:554), Simon et al. (1994:480) and Choudhary and Doraiswamy (1971:55).

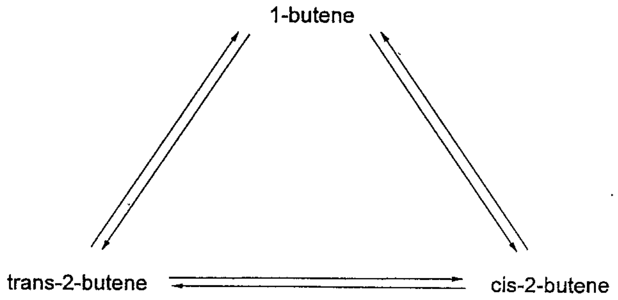


Figure 2.4 : Kinetic model for butene bond isomerisation (Ochoa and Santos, 1995:286)

This approach, to treat the linear butenes as a single, pseudo-component, was also used during this study as the actual partial pressure ratios of the linear butenes in the product gas were found to be similar to those predicted from thermodynamics. This suggests, as discussed in detail in Chapter 4, Section 4.2 that the double bond isomerisation activity of the catalyst is thermodynamically as opposed to kinetically limited. The result obtained by Szabo et al., (1993:329) who found that the inter-conversion amongst the linear butenes was not effected by the activity of the catalyst, may also be explained in this way. For a detailed discussion of the performance of the catalyst see Chapter 4. Details of both the skeletal and bond isomerisation mechanisms and the thermodynamics are given in Section 2.4 and Section 2.3.6, respectively.

The formation of by-products has also been extensively investigated. Choudhary and Doraiswamy (1971:230) found that the by-products consisted mainly of C_3 and C_5 hydrocarbons which they assumed were formed via the dimerisation of isobutene, followed by cracking to the various by-products. This is the same conclusion reached, by among others, Houžvička et al. (1996:288) and Mériaudeau et al. (1997:L1).

Bianchi et al. (1994:556), feeding pure isobutene obtained n-butene as the main product even at conversion levels as high as 50 %. From this, and their kinetic data, they concluded that the by-products were formed exclusively via the n-butenes. This was further confirmed by Cheng and Ponec (1994:345), who feeding n-octene obtained the characteristic by-products and by Simon et al. (1994:485) from an examination of the composition of the polymer stream. Only Szabo et al. (1994:323) proposed a dimerisation

/ cracking mechanism involving both the n-butenes and isobutenes. In view of the above, the overall reaction scheme as previously proposed in Figure 2.3 may be simplified to that shown in Figure 2.5 below.

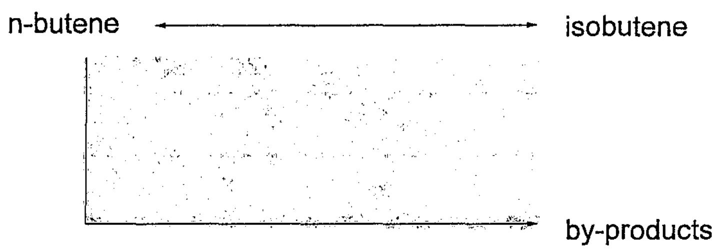


Figure 2.5 : Simplified butene reaction pathways

2.3.4 THERMODYNAMIC FEASIBILITY

To complete the examination of the reactions of the butenes, the thermodynamic feasibility of the various reactions shown in Figure 2.3 were determined. At a temperature of 750 K, the approximate average of the temperatures most often used in the literature for the skeletal isomerisation of the butenes, the free energy of formation ($\Delta_R G^\circ_{750K}$) and for the sake of completeness the heat of reaction ($\Delta_R H^\circ_{750K}$) were calculated. The necessary data was obtained from Stull (1969). Free energies of formation of less than zero, indicative of a thermodynamically favoured reaction, were obtained for the hydrogenation and cracking reactions and to a lesser extent for the skeletal and bond isomerisation reactions. Richardson (1980:92) proposed that a reaction is only thermodynamically feasible, with good equilibrium conversions possible if, $\Delta_R G^\circ_T$ is less than -10 kcal·mol^{-1} (-41.9 kJ·mol^{-1}). According to this proposal, the formation of the C_4 dimers is thermodynamically not favoured. As the route for by-product formation is via the dimers, this may in part explain why the formation of by-products, is generally negligible. Alternatively, the inclusion of a thermodynamically disfavoured intermediate may not be limiting, as its rapid conversion may pulls the entire cycle along. These proposals have to be considered while reviewing the literature on the mono- and bi-molecular mechanisms, as discussed in Section 2.4.

TABLE 2.1 : FREE ENERGY AND HEATS OF REACTIONS

Reaction	$\Delta_R G^\circ_{750K}$, kJ·mol^{-1}	$\Delta_R H^\circ_{750K}$,kJ·mol^{-1}
Bond isomerisation		
1-butene → *cis*-2-butene	-1.67	-9.59
1-butene → *trans*-2-butene	-4.19	-11.34
cis-2-butene → *trans*-2-butene	-2.51	-1.76
Skeletal isomerisation		
1-butene → isobutene	-8.29	-16.16
cis-2-butene → isobutene	-6.61	-6.57
trans-2-butene → isobutene	-4.10	-4.81
Hydrogenation		
1-butene → n-butane	-28.30	-132.78
cis-2-butene → n-butane	-26.62	-123.19
trans-2-butene → n-butane	-24.11	-121.44
isobutene → isobutane	-16.91	-122.48
'Dimerisation'		
1-butene → 1-octene	26.92	-78.70
cis-2-butene → 1-octene	30.26	-59.52
trans-2-butene → 1-octene	35.29	-56.01
isobutene → 1-octene	43.49	-46.38
'Cracking'		
1-octene → propene + 1-pentene	-28.46	78.61
1-octene → ethene + 1-hexene	-11.51	91.09
1-octene → isobutene	-43.49	46.38
1-butene → ethene	5.11	103.60
cis-2-butene → ethene	6.78	113.19
trans-2-butene → ethene	9.29	114.95
isobutene → ethene	13.40	119.72

As the hydrogenation of the butenes is thermodynamically very feasible at these conditions, potential catalyst should not contain a hydrogenation / de-hydrogenating function as this would lead to the formation of paraffins as opposed to the desired iso-olefins. That a hydrogenation or dehydrogenation function is not required for the isomerisation reaction or by-product formation was previously confirmed by Bianchi et al. (1994:557) and Simon (1994:485), who co-feeding hydrogen found no significant change in the isobutene or by-product formation rates. Bianchi et al. (1994:557) did observe hydrogen as a product during the conversion of the n-butenes to isobutene over a B/Al-BETA zeolite, but their data suggested no direct correlation between the isobutene formation and hydrogen production rates. They concluded that the hydrogen was formed via dehydrogenation during the formation of by-products. Furthermore, co-feeding hydrogen, had no effect on the isobutene formation rate, confirming that hydrogen does not participate in the bond and / or skeletal isomerisation mechanism of the butenes. This result was also confirmed during this study, as discussed in Chapter 4, Section 4.3.

2.3.5 HEATS OF REACTION

Shown in Figure 2.6 are the heats of the skeletal isomerisation reactions ($\Delta_R H^\circ_T$) calculated from the heats of formation $\Delta_F H^\circ_T$ (Stull, 1969:314), as a function of the temperature.

Szabo et al. (1993:329), while investigating the kinetics of both the bond and skeletal isomerisation reactions, found that the direct conversion of 1-butene to isobutene, as opposed to the conversion of *cis*-2-butene and *trans*-2-butene to isobutene, does not take place. Hence, as the heats of reaction of the latter two transformations are less than 2 kcal/mol (8.4 $kJ \cdot mol^{-1}$) above 773 K, the lower limit of the temperature traditionally used for the skeletal isomerisation reaction (See also Section 2.3.6), it may be assumed that the skeletal isomerisation reaction of the n-butenes to isobutene is thermally neutral. Using an average heat of reaction of 2 $kcal \cdot mol^{-1}$ (8.4 $kJ \cdot mol^{-1}$) and assuming that the thermodynamic equilibrium is reached, the adiabatic temperature rise was calculated (see Appendix 4), at the base case conditions, see Chapter 3, Section 3.5, to be 9.1 K.

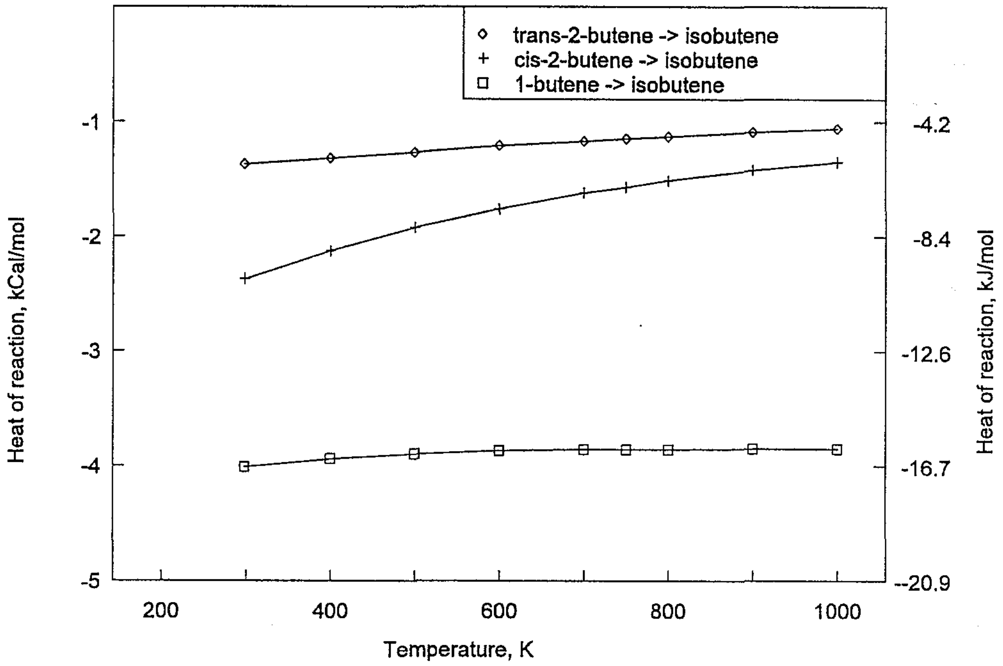


Figure 2.6 : Temperature dependency of the heats of isomerisation of 1-, *cis*-2- and *trans*-2-butene to isobutene

Other thermodynamic properties such as the heat content, free energy function, entropy and the heat capacity of the four isomers of butene, over a temperature range from 298 K to 1500 K, are given by Kilpatrick and Pitzer (1946:170), as well as Pitzer (1937:477) while the heats of combustion, formation and isomerisation are also given by Prosen et al. (1951:109) and Maslov (1954:352).

2.3.6 THERMODYNAMIC EQUILIBRIA

The equilibrium concentration of the reversible isomerisation of 1-butene to isobutene over a temperature range of 265°C to 425°C was studied by Serbryakova and Frost (1937:123). They recorded a decrease in the isobutene concentration with increasing temperature. A more detailed study, including all the isomers of butene was carried out by Kilpatrick et al. (1946:559), who came to the same conclusion. This suggests, in order to maximize the isobutene yield, the reaction temperature should be held as low as possible. It was however found by Frost et al. (1936:373) that below 300°C the reaction products consisted mainly of the oligomers of butene. Choudhary and Doraiswamy (1975:227) recorded bond and skeletal isomerisation activity between 300°C and 550°C, with cracking being the main reaction at higher temperatures. The temperature limits were also studied by Tung and Mcininch (1964:233) who found that 1-butene isomerisation proceeds in stages. At lower temperatures only bond isomerisation was observed, with the products reaching equilibrium composition at approximately 200°C. This equilibrium composition prevails until 310°C when isobutene was first detected. The concentration of isobutene continues to increase with temperature until at about 475°C cracked products were first observed. It was concluded by them that these limits are valid for most acidic catalysts suitable for butene skeletal isomerisation.

The results recorded by Kilpatrick et al. (1946:559) as reported by Fakas (1950:398) are reported in Table 2.2 below. Also shown in Table 2.2 are the equilibrium compositions calculated using two process engineering modelling packages, Pro II and AspenPlus. An examination of the data shown in Table 2.2 shows that the calculated isobutene content of the products at equilibrium is always higher than the values measured by Kilpatrick et al. (1946:559) while the 1-butene content is always lower. Furthermore, different thermodynamic equilibrium compositions were predicted by the two engineering modelling packages used. In view of the uncertainty surrounding the thermodynamic equilibrium composition of the four butene isomers, the conservative measured, as opposed to the calculated values, were used during this study. The measured thermodynamic equilibrium composition of the four isomers over a temperature range of 200°C to 1000°C is shown in Figure 2.7

2.3.7 EQUILIBRIUM CONSTANT

Of course, if the products are at thermodynamic equilibrium, then the ratio of the forward (k_1) to reverse (k_2) reaction rate constants, i.e., the equilibrium constant, K_p may be calculated from the ratios of the product (p_{prod}) and feed (p_{feed}) partial pressures in the flue gas.

TABLE 2.2 : BUTENE THERMODYNAMIC EQUILIBRIUM COMPOSITIONS

Temperature, °C	isobutene, %	*trans*-2-butene, %	*cis*-2-butene, %	1-butene, %
Kilpatrick et al. (1946:559)				
400	41.24	26.23	18.11	14.43
500	37.30	25.13	18.56	19.03
520	**36.62**	**24.89**	**18.59**	**19.91**
540	35.97	24.66	18.60	20.87
560	35.35	24.43	18.61	21.63
580	34.75	24.20	18.60	22.46
600	34.18	23.97	18.58	23.28
800	29.57	21.95	18.06	30.49
Calculated using Pro II				
400	48.89	25.52	15.89	9.70
500	44.53	25.86	16.79	12.82
520	**43.85**	**25.86**	**16.88**	**13.41**
540	43.17	25.86	16.98	14.00
560	42.49	25.86	17.07	14.59
580	41.82	25.84	17.16	15.18
600	41.14	25.84	17.25	15.77
800	36.21	25.34	17.47	20.99
Calculated using AspenPlus				
400	46.30	22.80	17.50	13.40
500	41.10	23.10	18.40	17.40
520	**40.30**	**23.10**	**18.50**	**18.10**
540	39.40	23.10	18.60	18.90
560	38.60	23.10	18.70	19.60
580	37.90	23.10	18.70	20.30
600	37.10	23.10	18.80	21.00
800	31.50	22.50	18.80	27.70

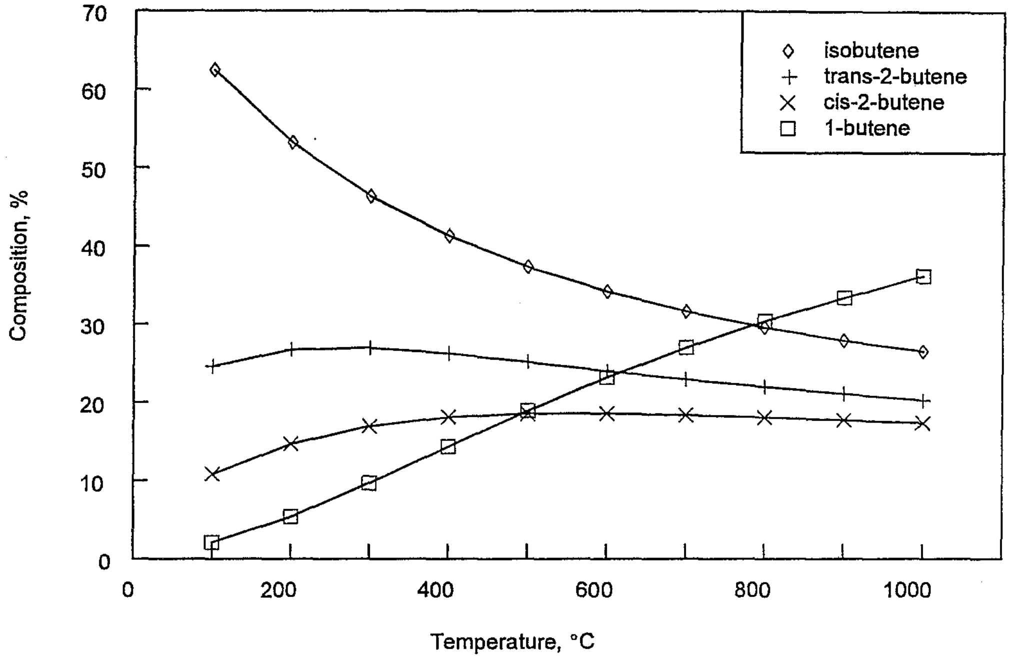


Figure 2.7 : Equilibrium concentration of the isomers of butene (Farkas, 1950:398)

At equilibrium

$$K_p = \frac{k_1}{k_2} = \frac{p_{prod}}{p_{feed}} \qquad 2.1$$

Various procedures to calculate the equilibrium constants and hence the thermodynamic equilibrium composition of the butene isomers may be found in the literature. Frost et al. (1936:375) found that over a temperature range of 265°C to 426°C, the equilibrium constant could be approximated using

$$\log K_p = \log\left(\frac{\text{isobutene}}{\text{n-butene}}\right) = \frac{304}{T} - 0.528 \pm 0.02 \qquad 2.2$$

where

K_p is the equilibrium constant and
T is the temperature, °C.

The equilibrium constants may also be calculated from the tables and nomographs given by Destremps et al. (1961:46) over temperatures from 0 to 1950°C, or by using the Gibbs free energy reported at various temperature between 298 K to 1000 K by Stull (1969:245) and the relationship between the equilibrium constant and the Gibbs free energy (Smith and van Ness, 1981:385).

2.3.8 ACTIVATION ENERGY

Little information is available in the literature on the kinetics of the skeletal isomerisation of the n-butenes to isobutene. Pis'man and co-workers (1965, 1968), as reported by Choudhary and Doraiswamy (1975:227) examined the kinetics of this reaction over a fluorinated alumina catalyst. However, their work was limited to the determination of the activation energy which for the forward reaction was found to be 21 $kcal \cdot mol^{-1}$ (87.9 $kJ \cdot mol^{-1}$) and for the reverse reaction 22.7 $kcal \cdot mol^{-1}$ (95 $kJ \cdot mol^{-1}$). Nilsen et al. (1986:341), reported an activation energy of 16.2 $kcal \cdot mol^{-1}$ (67.8 $kJ \cdot mol^{-1}$) over an alumina catalyst and values of 18, 25.1, 25.5, 24.7 and 27 $kcal \cdot mol^{-1}$ (76.39, 105.07, 106.74, 103.39 and 113.02 $kJ \cdot mol^{-1}$) for alumina catalysts with silica contents of 3.3, 2.49, 1.65, 1.12 and 1.04 mass %, respectively. Values ranging from 13.1 $kcal \cdot mol^{-1}$ (54.8 $kJ \cdot mol^{-1}$) to 15 $kcal \cdot mol^{-1}$ (62.8 $kJ \cdot mol^{-1}$) were reported by Bianchi et al. (1994:554) using a boro-aluminosilicate zeolite, while Choudhary and Doraiswamy (1975), using a fluorinated alumina catalyst reported a value of 8.4 $kcal \cdot mol^{-1}$ (35 kJ/mol). During their work external factors such as heat and mass transfer effects were avoided by using a spinning basket reactor and suitable stirrer speed and pore diffusion eliminated by using catalyst particles of 40 to 60 mesh, i.e., an average particle size of 0.034 cm (Choudhary and Doraiswamy, 1975:228). Surprisingly, values below 10 $kcal \cdot mol^{-1}$ (41.9 kJ/mol) which are normally considered to be an indication that mass transfer resistances have not been eliminated, for the bond isomerisation of various olefinic and skeletal isomerisation of various paraffinic hydrocarbons were previously reported in the literature. A summary of these as reported by Condon (1958:134) are given in Table 2.3 below.

TABLE 2.3 : ACTIVATION ENERGIES (E) - ISOMERISATION REACTIONS

Feed	Product	Catalyst	E, kJ·mole^{-1}
n-butane	isobutane	$AlBr_3$-HBr	38.5
n-butane	isobutane	$AlCl_3$-HCl	40.0
3-methyl pentane	2-methyl pentane	H_2SO_4-99.8 %	26.8
2,3-dimethyl pentane	2,4 dimethyl pentane	H_2SO_4-99.8 %	20.5
(+)3-methyl hexane	dl-3-methyl hexane	Ni-kieselguhr	108.8
cyclohexane	methyl cyclo pentane	MoS_2	148.2
cis-2-butene	*trans*-2-butene	Ni-porcelain	16.7
cis-2-butene	*trans*-2-butene	Ni (H_2 or D_2)	22.2
cis-2-butene	*trans*-2-butene	Thermal	75.3
trans-2-butene	*cis*-2-butene	Ni (H_2 or D_2)	20.1
1-butene	2-butene	Ni (H_2)	24.7
1-butene	2-butene	Ni (H_2)	20.9
1-butene	2-butene	Ni (D_2)	32.7
1-butene	2-butene	$70P_2O_5$-$30H_2O$	67.8
1-butene	2-butene	$76P_2O_5$-$24H_2O$	55.7
1-butene	2-butene	$80P_2O_5$-$20H_2O$	45.6
1-butene	2-butene	$97P_2O_5$-$3H_2O$	32.7
2-ethyl-1-hexene	methyl heptenes	SiO_2	39.3
p-xylene	m-xylene	HF-BF_3	53.2
p-xylene	m-xylene	HBr-$AlBr_3$	89.2
o-xylene	m-xylene	HBr-$AlBr_3$	95.4

2.3.9 KINETICS STUDIES

The classical approach to kinetics of heterogeneous catalytic systems is to make the assumption that one single reaction step is rate determining, and that all other steps are regarded as fast quasi equilibrium steps (Salmi 1986,1987) A Langmuir Hinshelwood

Hougen Watson or semi empirical rate equation can be derived by substitution of stoichiometric relationships into the proposed rate determining step. In the n-butene skeletal isomerisation reaction, these are normally functions of the n-butenes and the isobutene. Discrimination between rival models is done statistically by fitting the derived rate equation to the experimental data and selecting the best fit and models that do not satisfy the statistical criteria within a desired degree of accuracy are discarded (Froment, 1987).

Using this approach, a detailed kinetic investigation was conducted by Choudhary and Doraiswamy (1975:227) in an attempt to explain the skeletal isomerisation of the n-butenes to isobutene. Using a fluorinated eta-alumina catalyst, containing 1 mass % fluorine, they attempted to develop a Hougan-Watson (Langmuir Hinshelwood) type rate model. The necessary data was collected using a rotating basket, continuous stirred gas-solid reactor which, according to Choudhary and Doraiswamy (1972:420), gave the most reproducible results when compared to other gradientless reactors. During their work external factors such as heat and mass transfer effects were avoided by using a suitable stirrer speed and pore diffusion eliminated by using catalyst particles of 40 to 60 mesh, i.e., an average particle size of 0.034 cm (Choudhary and Doraiswamy, 1975:228). The kinetic investigation of the reaction was conducted at temperature between 300°C to 435°C at a total pressure of 0.92 atm, a butene flow rate of 0.2 to 0.7 $g \cdot mole \cdot hr^{-1}$ and a space time of between 3 and 20 $g \cdot hr \cdot gmol^{-1}$. Choudhary and Doraiswamy, (1975:228) assumed that the inter-conversion of the linear butenes was much faster than the skeletal rearrangement. Hence, they treated the linear butenes as a single pseudo-species, namely n-butene. Furthermore, they proposed that the by-products were formed exclusively via the oligomerisation of isobutene followed by cracking. The overall reaction could thus be represented as

$$\underset{(A)}{\text{n - butene}} \underset{k_{BA}}{\overset{k_{AB}}{\rightleftarrows}} \underset{(B)}{\text{isobutene}} \xrightarrow{k_{BC}} \underset{(C)}{\text{poly isobutene}} \tag{2.4}$$

with the overall rate of formation of isobutene (r_B) being

$$r_B = r_{AB} - r_{BA} - r_{BC} \qquad 2.5$$

and poly isobutene (r_C) being

$$r_C = r_{BC} \qquad 2.6$$

A small conversion (< 1 %) due to cracking was also observed but was found to be mostly due to homogeneous cracking. This side reaction was thus ignored during the kinetic investigation. Using a statistical design procedure, they found that the model which best fitted the observed data, over a temperature range of 300°C to 400°C was the Hougan-Watson type kinetics, with the rate controlling step being the adsorption of 1-butene on a single site. This model takes the form

$$r_B + r_C = \frac{k \cdot (p_A - p_B/K)}{(1 + K_B \cdot p_B)} \qquad 2.7$$

where

r_B	is the rate of formation of isobutene, gmole·hr^{-1}·g^{-1},
r_C	is the rate of conversion of isobutene to poly isobutene, gmole·hr^{-1}·g^{-1},
k	is the rate constant, gmole·hr^{-1}·g^{-1}·atm^{-1},
P_A	is the partial pressure of n-butene, atm,
P_B	is the partial pressure of isobutene, atm,
K	is the equilibrium constant, - and
K_B	is the adsorption equilibrium coefficient for isobutene, -.

At 435°C and higher temperatures they found that a switch in the mechanism occurred, to one where the desorption of isobutene became the rate controlling step. The corresponding model using the same nomenclature as before is

$$r_B + r_C = \frac{k \cdot (p_A - p_B/K)}{(1 + K_A \cdot p_B)} \qquad 2.8$$

where

K_A is the adsorption equilibrium coefficient for n-butene, -.

However, while examining the significance of the adsorption terms, Choudhary and Doraiswamy (1975:234) found that the kinetic data could also be represented by a first order mass action law, as shown below.

$$r_B + r_C = k \cdot (p_A - p_B/K) \qquad 2.9$$

The Hougan-Watson type model could however not be rejected, as on a statistical basis no distinction between the various models was possible.

To prove that a particular mechanism is the correct one, it must be shown that the family of curves representing the favoured mechanism fit the experimental data better than the other families, so that these can be rejected. With the large number of parameters involved, between 3 to 7, that can be chosen arbitrarily for each rate controlling step, an extensive experimental program would be required with very precise and reproducible data. It is not good enough to select the mechanism that best fits the data as differences may be so small as to be explained in terms of experimental error or statistical insignificance. In most cases the magnitude of the experimental error masks the differences predicted by the various mechanisms and so any number of alternative mechanisms may fit the data equally well. Hence, we can only select the mechanism which best fits the data with no guarantee that it is the correct mechanism, making it difficult to justify the extent of the work required. It may however be argued that once the correct mechanism has been found, the performance of the catalyst at previously untried operating conditions can be predicted. However this is still dangerous as other resistances may become important, in which case the original rate equation is no longer valid. With this in mind, the approach used by Choudhary and Doraiswamy (1975:234), in evaluating on a statistical basis not only the feasibility of the Hougan Watson type rate equations but the law of mass action as well, seems the correct one.

That the n-butene isomerisation rate could adequately be represented by a first order power law kinetics was demonstrated previously. Nielsen et al. (1986:341), operating at 475°C with alumina and silica alumina catalysts, obtained straight lines when plotting the reaction rates vs the n-butene partial pressures from 0 to 1 atm. This was later confirmed by Bianchi et al. (1994:556), who using between 0.1 and 0.3 g of a boro aluminosilicate zeolite and gas flow rates at one atmosphere in the range of 5 to 500 $cm^3 \cdot min^{-1}$, which permits work under differential conditions with conversion less than 10 %, obtained a linear relationship between the isobutene formation rate and the n-butene partially pressure, at 500°C, confirming that the former is first order in n-butene.

Based on the results obtained during the inter-conversion of the isobutene to n-butene, which showed that the reaction is indeed reversible and that the by-products are formed exclusively via the linear butenes, Bianchi et al. (1994:556) propose a simple reaction scheme. Treating the linear butenes as a single pseudo-species, n-butene, and assuming that the coverage of the catalyst surface is proportional to the n-butene partial pressure, they propose an overall reaction scheme as shown in Equations. 2.10 and 2.11 below. See also Section 2.3.3 for further justification for using this simplified reaction scheme.

$$\underset{(A)}{\text{n-butene}} \underset{k_{BA}}{\overset{k_{AB}}{\rightleftarrows}} \underset{(B)}{\text{isobutene}} \qquad 2.10$$

and

$$\underset{(A)}{\text{n-butene}} \xrightarrow{k_{AC}} \underset{(C)}{\text{by-products}} \qquad 2.11$$

They further found that the formation of by-products could be represented by means of a simple power law. Hence, using a mass action law rate equation for the n-butene skeletal isomerisation reaction, as was previously proposed by Choudhary and Doraiswamy (1975:234), Equation 2.9, together with a power law in terms of n-butene to account for the by-product formation, the global rate of disappearance of the n-butenes to isobutene and the by-products, can be represented by

$$-r_A = \left(k_{AB} \cdot p_A - k_{BA} \cdot p_B\right) + k_{AC} \cdot p_A^n \qquad 2.11$$

with the order of the by-product formation reaction, specifically the rate of production of propene, being n = 1.5.

In a separate study conducted by Szabo et al. (1993:322) the linear butenes were not considered to be a single entity and the rates of bond and cis-trans isomerisation included in the kinetic scheme. The investigation was conducted in a plug flow reactor using between 0.05 and 1.5 g of a fluorinated alumina catalyst, containing 1.6 mass % fluorine, at a temperature of 450°C and atmospheric pressure, a butene flow rate between 0.35 and 2.8 $g \cdot hr^{-1}$ and a space times of between 0.05 and 1.5 $g \cdot hr \cdot g^{-1}$. Water was co-fed to improve the selectivity to isobutene and to reduce the rate of deactivation. The resultant butene and water partial pressures at the reactor inlet were 9.8 kPa(a) and 2.3 kPa(a) respectively with the balance being nitrogen.

The reactions that were considered to take place were those shown previously in Figure 2.3, with all the by-products considered to be a single pseudo-species formed via the condensation of the n-butenes with isobutene followed by cracking to lighter and heavier products. Considering the reactions to be elementary, and the rate first order, Szabo et al. (1993:323) set up a set of five differential equations to describe the changes in concentration with space time of the various isomers of butene and side products. Assuming ideal gas behaviour, in that the activities are proportional to the concentrations, and hence making use of the equilibrium relationships amongst the butenes, the number of independent rate constants could be reduced from a total of thirteen to seven.

After suitable manipulation of their data, they concluded that the reactions take place in three stages. Fast double bond migration together with cis-trans isomerisation (I), skeletal isomerisation to isobutene, (II) and the formation of side products (III). Evidence for the direct conversion of 1-butene to isobutene could not be found. Examining the catalyst activity as a function of the time on line, Szabo et al. (1993:325) found that the rates of skeletal isomerisation and secondary products formation decrease, while the rate of double bond and cis-trans isomerisation did not change with the time on line. In fact the selectivity could simply be related to the overall conversion regardless of time on stream. Catalyst deactivation was attributed by them to carbon deposition during the bi-molecular reactions between n-butenes and isobutene in the formation of by-products.

The fact that the overall rate of the n-butene skeletal isomerisation reaction to isobutene may be controlled by several reaction steps, was not considered by these workers.

2.3.10 MULTI-STEP KINETIC MODELLING

In catalytic systems the overall rate of reaction is comprised of adsorption, surface reaction and desorption steps. Complex reaction mechanism may be simplified by assuming one single rate determining step, or by applying the concept of a most abundant surface intermediate. The overall rate may in fact be controlled by several reaction steps (multiple rate control) and may further be complicated if different steps are controlling at different operating conditions. In such cases feed composition, conversion levels, temperature, etc., will determine which steps will be rate limiting. Other instances where the assumption of a single rate controlling step can not be made are when the reactor is operated under transient conditions, if the catalytic reaction exhibits steady state multiplicity or periodic oscillations (Salmi, 1987). The multi-step approach in modelling the n-butene skeletal isomerisation reaction has not previously been reported in the literature.

Computer modelling of non-analytical multi-step kinetic models is complicated by an increased number of parameters, that normally have to be evaluated using non-linear regression techniques. If the number of model parameters to be estimated becomes large, computational time may become a serious problem. For this reason non-analytical multi-step modelling have greatly been avoided in the past. However, with computers becoming faster all the time, non-analytical multi-step models can now be solved which before were only of theoretical importance. In the past the aim of kinetic modelling was to select the correct rate determining step and to develop a single rate equation. Senkan is of the opinion that today the opposite is true, i.e., that mechanisms may not be detailed enough and potentially important elementary reactions may have been overlooked.

The rate equations previously considered were analytical rate equations derived from LHHW principles with the assumption of one rate limiting step. A fair number of non-analytical multi-step kinetic modelling may be found in the literature, although not applied to the n-butene skeletal isomerisation reaction. Examples include the gas phase pyrolysis of CH_3Cl to C_2 hydrocarbons (Karra and Senkan, 1988), soot formation in C_2H_2 combustion (Frenklachet al 1986) or the direct oxidation of CH_4 to H_2 and CO in O_2 (Hickman and Smidt, 1993).

Sensitivity and reaction path analyses are essential elements in any multi-step kinetic model and this is stressed by Senkan (1992). The sensitivity analysis provides a way to assess the limits of confidence that may be put on model predictions. The major reaction pathways responsible for the reagent consumption and product formation can be identified by reaction path analyses and reactions which have the largest impact on the model output are regarded as the important reaction steps. Sensitivity and reaction path analysis are techniques by which possible reaction steps in a mechanism may be ranked in order of importance. Important reaction steps can be identified and less important once may be disregarded. Discarding of reaction steps should be handled with care as it must be kept in mind that reaction steps which are not important under one set of operating conditions may become important under another set of operating conditions.

Another aspect of the approach of multi-step or any form of kinetic modelling to keep in mind is that when the objective of the modelling effort is the validation of a reaction mechanism, the major uncertainty in the model must reside in the kinetic reaction mechanism. To ensure this the process must either be studied in the absence of transport phenomena or the transport phenomena must be modelled in a very precise manner. Various criteria are available to determine the extent to which transport phenomena in and around the catalyst particle and the extent of deviation from ideal plug flow are available. See also Chapter 5 and Appendix 4.

2.3.11 FIXED BED REACTOR MODELLING

In view of the importance of heterogeneous catalytic reactions in industry, the need for the development of mathematical models is obvious. Such models may be used to supplement experimental data, plan experimental work, design new reactors and to optimise existing commercial units. In certain applications, mathematical models may also be used for process control purposes. In complex catalytic systems the models have to be simplified to the extent where an acceptable balance is reached between the accuracy of the model and the cost in terms of development and operation of the computer program. Cresswell and Patterson, 1970). The availability of modern high speed computers has certainly contributed to the broadening in the field of applied mathematical modelling over recent years.

Different fixed bed models have been proposed in the past for all kinds of applications. These models vary from the simplest pseudo-homogeneous one-dimensional models, all called plug flow models, to complex heterogeneous two-dimensional models. The best model is obviously the one which describes all the physical and chemical processes occurring inside the reactor, but simplifications are not only convenient but often also necessary to limit numerical cost time (Baiker and Epple, 1986). Criteria to discriminate between different models are available in the literature and are discussed in Chapter 5.

The fixed bed reactor models have been classified by Froment (1984). All models belong to one of four groups

1 one-dimensional pseudo-homogeneous
2 two-dimensional pseudo-homogeneous

3 one-dimensional heterogeneous
4 two-dimensional heterogeneous

Different non plug flow mechanisms play a role in the mass and heat transfer in packed beds, and lumping of these mechanism to obtain effective diffusion and conduction terms lead to the so called pseudo-homogeneous models. These models do not discriminate between the solid and the fluid phase. Both temperature and concentrations on the catalyst surface are set equal to the temperature and concentrations of the bulk fluid. Contrary to this the heterogeneous models discriminate between the solid and the fluid phases with heat and mass transfer relationships linking the differential equations in the two phases. The models are further classified into one and two-dimensional models. The one-dimensional models ignore radial temperature and concentration profiles whereas these are accounted for in the two-dimensional models. Axial dispersion and intra-particle gradients may also be included if necessary.

The mathematical equations for all the models which were mentioned are obtained by setting up the mass and energy balance over a differential element of the reactor, which is subsequently integrated over the length of the reactor tube. Mass balances for all the chemical species are required, although the flow rates of some of the components (usually products) can often be calculated from stoichiometric relationships. The differential equations for all models are well described in the literature and will not be repeated here (Froment and Bischoff, 1979; Smith, 1981, Levenspiel, 1972, Mulder, 1985). In the present study, both a one-dimensional and two-dimensional, to quantify the significance if the radial temperature profile, pseudo-homogeneous models were used. For details of the procedure used, see Chapter 5, Appendices 3 to 5 and Keyser, (1996:2-20).

2.4 ISOMERISATION MECHANISM

There are five types of isomerisation reactions that may be identified (Condon, 1958:98). These, in order of increasing difficulty, are :

1. Cis - trans isomerisation
2. Double bond shift at a chain branch
3. Double bond shift in a branchless chain
4. Skeletal isomerisation without change in the maximum chain length
5. Skeletal isomerisation with a change in the maximum chain length

In the case of butene isomerisation, only types 1, 3 and 5 are relevant. Type 2 may occur but the products could not be distinguished from the feed unless the various atoms were labelled, while type 4 cannot occur. The skeletal and bond isomerisation of the butenes may be achieved over a variety of heterogenous catalytic systems each with its corresponding mechanism. Three mechanisms have been proposed for various catalytic schemes (Goldwasser and Hall, 1981:53). These are:

1. an allylic (anion) mechanism for basic catalysts
2. an atomic free radical mechanism which incorporates the associative and hydrogen switch mechanism over metals and organo- metallic systems
3. a cation mechanism over acidic catalysts

A brief discussion of the various isomerisation mechanism is now presented with an emphasis on the cation mechanism, specifically the mono- and bi-molecular cation mechanisms over acidic catalysts, as used during this study.

2.4.1 ANION MECHANISM

Over a basic oxide catalyst, such as ZnO, proton transfer from 1-butene to a surface oxygen ion may occur. This will lead to the formation of an allylic anion associated with the (paired) cation exposed at the anion vacancy on the surface. The formation of two allylic species are possible, these being the syn- and the more stable anti-π-allyl configuration. Inter-conversion of the two species takes place via the σ-allyl configuration. As *cis*-2-butene can only be formed via the more stable anti-π-allyl, and *trans*-2-butene via the less stable syn-configuration, high *cis* to *trans* ratios are expected and were indeed found by Goldwasser and Hall (1981:54). Basic oxide catalysts are however not capable of catalising skeletal isomerisation reactions (Condon, 1958:44).

2.4.2 FREE RADICAL MECHANISM

The free radical mechanism occurs over transition metal compounds which are ordinarily not considered to be acidic. As the activation of these catalysts usually involves a high temperature oxygen and hydrogen treatment, oxygen and protons may remain on the surface. The cation mechanism can thus not be ruled out entirely, but it seems unlikely due to the inability of these compounds to catalyse skeletal isomerisation reactions (Condon, 1958:103).

The free radical nature of these materials and hence the catalytic activity is associated with the unfilled d-orbitals of the metals. Alkenes may be adsorbed at one or both of the doubly bonded carbons via the equal division of the electrons to form a di-radical. Bond migration may now occur via one of the following mechanisms:

1. The dissociative mechanism
2. The associative mechanism
3. The hydrogen switch mechanism

2.4.2.1 THE DISSOCIATIVE MECHANISM

In the dissociative mechanism, the adsorption of the olefin occurs at an alpha carbon by a dissociative process, resulting in a M-H and M-C bond. A hydrogen atom already on the surface then adds to the opposite and of the double bond causing bond migration and desorption as shown in Figure 2.8(a).

2.4.2.2 THE ASSOCIATIVE MECHANISM

In the associative mechanism the olefin is adsorbed at the double bond. A hydrogen atom already on the surface adds to one end of the double bond while a hydrogen from the alpha carbon at the other end is adsorbed at another site as shown in Figure 2.8(b).

2.4.2.3 THE HYDROGEN SWITCH MECHANISM

In the hydrogen switch mechanism a carbon to metal bond is not formed. Instead a hydrogen atom on the surface of the metal is added to one end of the double bond while a hydrogen from the alpha carbon at the other end is simultaneously adsorbed at another site, as shown in Figure 2.8(c).

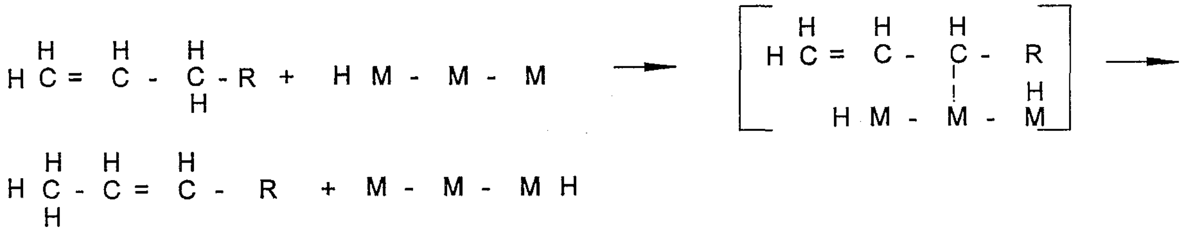


Figure 2.8(a) : The dissociative mechanism

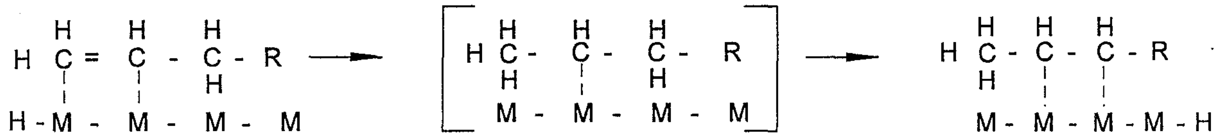


Figure 2.8(b) : The associative mechanism

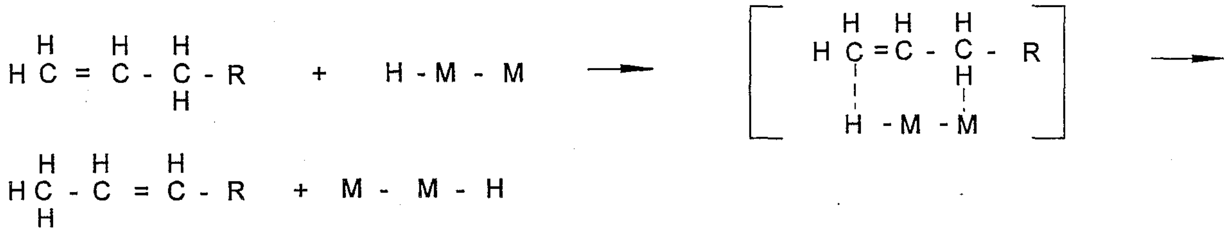


Figure 2.8(c) : The hydrogen switch mechanism

Figure 2.8 : Isomerisation mechanisms over electronic type catalysts (Condon, 1958:104)

2.4.3 CATION MECHANISM

The isomerisation of alkenes with acidic catalyst can generally be explained by means of a cation mechanism. The steps involved in such a mechanism, over a Brønsted acid type catalyst involve the addition of a proton from the acid site to the alkene, rearrangement of the so-formed cation followed by the transfer of a proton back to the catalyst. In the case of a Lewis acid the cation intermediate is generated via the sharing of a pair of electrons between the adsorbed olefin and the acid site, followed by rearrangement and desorption. It is for this reason, i.e., steric factors, that Lewis acids are limited to catalising bond isomerisation while Brønsted acids are capable of catalising both bond and skeletal isomerisation (Condon, 1958:44)

2.4.3.1 BOND ISOMERISATION OVER LEWIS ACID SITES

The bond isomerisation of the n-butenes over Lewis acids has been examined by a number of workers. However, some uncertainly still exists as to the structure of the intermediates. Peri (1965) as discussed by Gerberich and Hall (1966:107) suggested that the oxide and exposed aluminum on the surface of alumina act respectively as nucleophilic and electrophilic centres. This dual acid-base nature of the catalyst can result in either proton or hydride abstraction occurring on the surface. After examining the surface and molecular geometry, Gerberich and Hall (1966:108) concluded that if 1-butene in the cis-configuration approached the surface, it would be adsorbed via the terminal carbon atoms forming a cyclic intermediate. The strong electrostatic field surrounding the small cations would polarize the carbon to hydrogen bond (C^+H^-) effectively freezing the molecule in the *cis*-configuration. Due to the protophillic nature of the oxide ion, proton transfer from the allylic position to the terminal methylene group could occur as shown in Figure 2.9, and after desorption, cis-2-butene would be formed. This mechanism was also adopted by Ilie et al. (1985:6) who examined the bond isomerisation of the n-butenes over gamma-irradiated alumina. As formation of *trans*-2-butene is not possible according to this mechanism, they suggested a second mechanism involving the rotation around the $^-C{=}C^-$ bond until the thermodynamic equilibrium was reached.

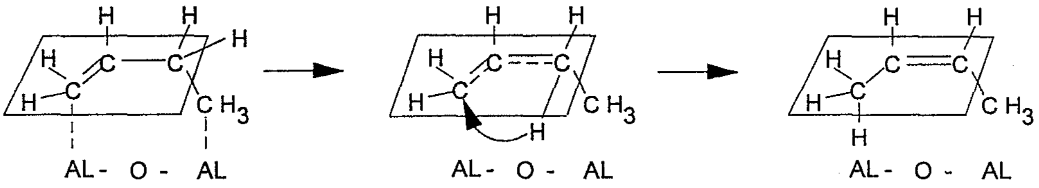
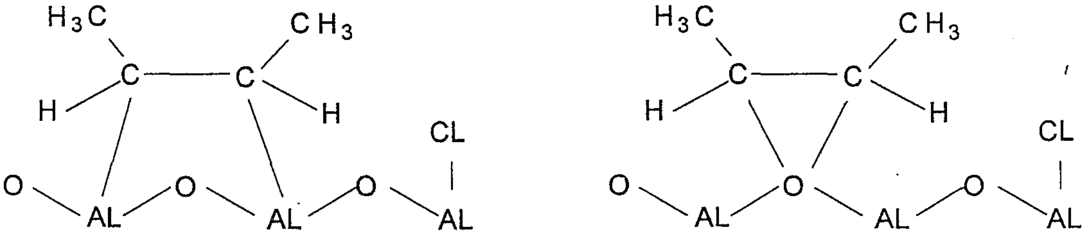


Figure 2.9 : Possible butene bond isomerisation mechanism (Ilie et al., 1985:6)

Alternatively the interaction of 1-butene in the *trans*-configuration may occur via the co-ordination of the π double bond orbital in 1-butene with "d" aluminum ion orbital. This would, however, require the involvement of another type of centre.

Ilie et al. (1985:7) further found the -C=C- bond of the chemisorbed 1-butene molecule on the surface of alumina was preserved, as determined by IR spectroscopy. This is in direct conflict with the results obtained by Ayame and Sawada (1989:3059) who, using the same technique, found that the chemisorbed 1-butene on chlorinated alumina completely lost its double bond character. According to Ayame and Sawada (1989:3056) 1-butene can be adsorbed on the surface of the catalyst in one of two species formed via an inter-molecular hydrogen transfer as shown in Figure 2.10. Examining the structure more closely they concluded that the form involving two centres, i.e., Form (I) would be favoured.



Form I

Form II

Figure 2.10 : Structure of adsorbed butene intermediates on chlorinated alumina (Ayame and Sawada, 1989:3056)

In an attempt to explain the mechanism by which these species are formed, they examined the nature of the acid site of chlorinated alumina using IR spectroscopy. From this they concluded that both hydroxyl groups and basic oxygen ions, with large electron clouds are not present on the catalyst surface. Consequently the 1-butene molecule can approach very closely to the strong Lewis site resulting in the attraction of a hydrogen atom on the allylic carbon, while the adjacent Lewis acid site attracts the terminal methylene carbon as shown in Figure 2.11

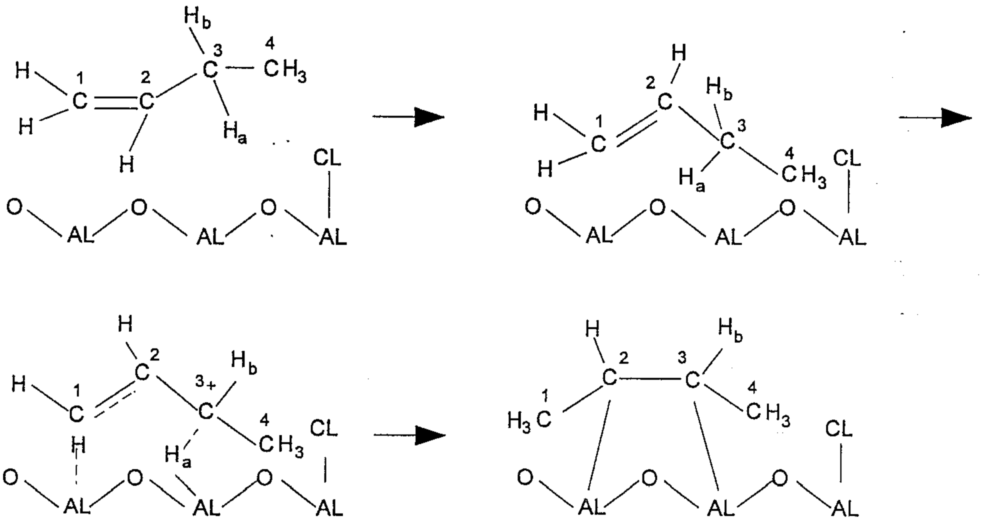


Figure 2.11 : Possible isomerisation mechanism on the chlorinated aluminas (Ayame and Sawada, 1989:3059)

Simultaneously the methyl group moves away from the surface due to its large electron cloud and the number 2 carbon moves upwards. After the shifting of π electrons the cis-configuration would be completed. Ayame and Sawada (1989:3059) go on to say that due to the absence of the double bond of the adsorbed species, the hydride shift and the ^{2}C-^{3}C carbon axis rotation takes place very fast. To explain the formation of *trans*-2-butene they suggest that at higher temperatures the doubly bonded intermediate could be re-arranged to a singly bonded σ-butyl cation, i.e. the *trans*- configuration.

2.4.3.2 BOND ISOMERISATION OVER BRØNSTED ACID SITES

A dual site mechanism with butene chemisorbed on the Lewis acid site and the hydroxyl group functioning as co-catalysts was proposed by Gerberich and Hall (1966:106) while studying the bond and skeletal isomerisation of the butenes over silica alumina. They proposed that the classical secondary butyl cation, formed in this manner, is adsorbed on the catalyst with the trigonal carbon atom, and the atoms surrounding it forming a plane parallel to the surface. This, as shown in Figure 2.12, is in accordance with the structure of the adsorbed species as proposed by Ozaki and Kimura (1964:404). The loss of a proton from position 1 would lead to the formation of *cis*-2-butene and from position 2 to *trans*-2-butene.

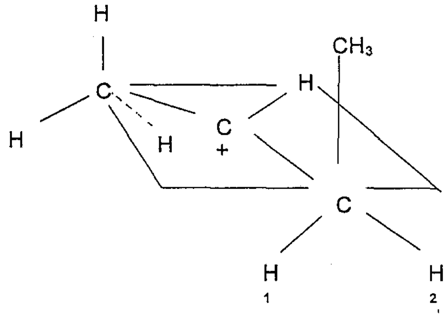
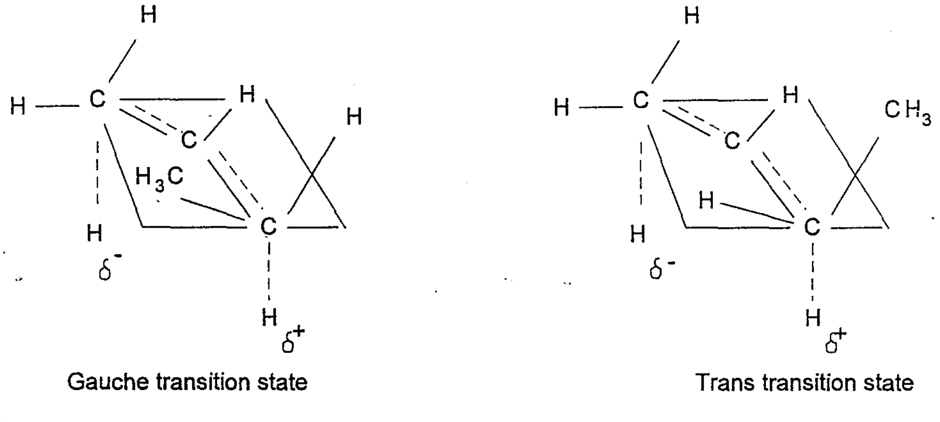


Figure 2.12 : Classical cation intermediate (Gerberich and Hall, 1966:107)

An alternative mechanism proposed by Gerberich and Hall (1966:107) is the hydrogen switch mechanism. They postulated that the different transition states could be formed as the 1-butene molecule approaches the surface of the catalyst. These are the *trans* form, if the methyl group eclipses the hydrogen atom on C-2, and the gauche form if the hydrogen atoms on C-2 and C-3 eclipse each other. Upon hydrogen switch the *trans* and *cis* isomers would be formed respectively as shown in Figure 2.13.



Gauche transition state

Trans transition state

Figure 2.13 : Gauche and trans transition states of butene intermediates (Gerberich and Hall, 1966:107)

According to both this and the previous mechanism the ratio of the *cis*- to *trans*-isomers should be approximately unity, as was found to be the case, by among others, Gerberich and Hall (1966:108).

2.4.3.3 SKELETAL ISOMERISATION OVER BRØNSTED ACID SITES

The cation mechanism for the overall reversible isomerisation of the n-butene to isobutene, as shown in Figure 2.14, was first proposed by Choudhary (1974:39), while studying the performance of a fluorinated alumina catalyst.

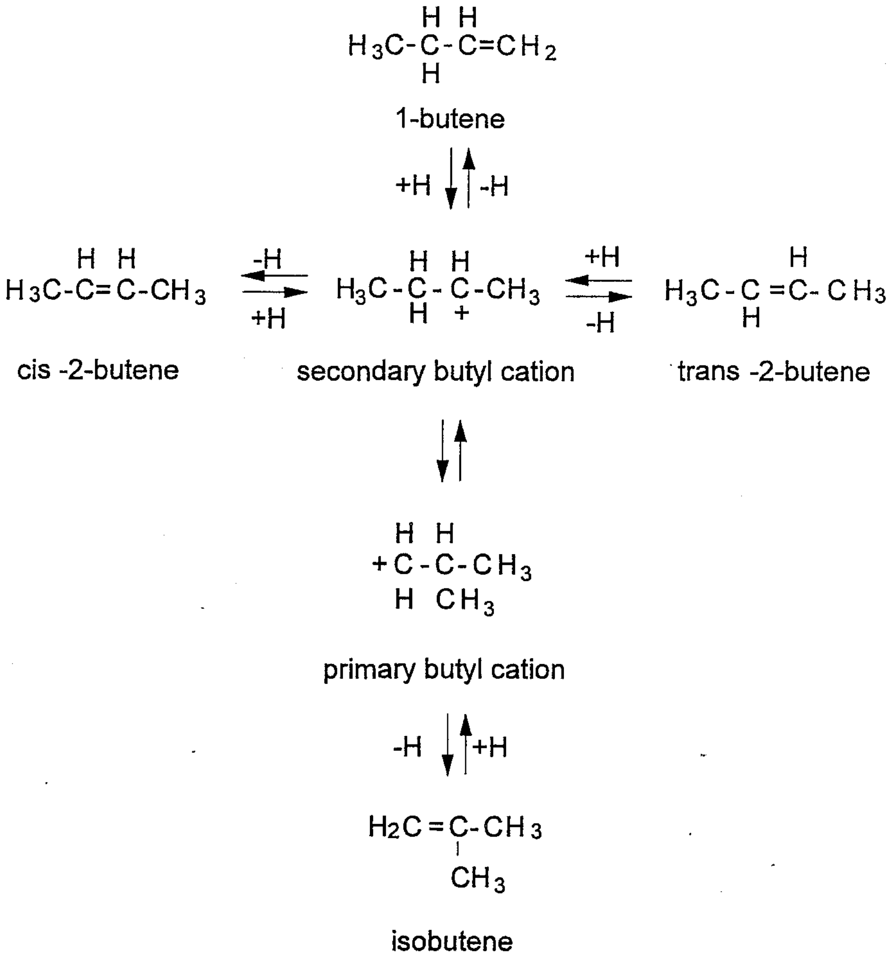
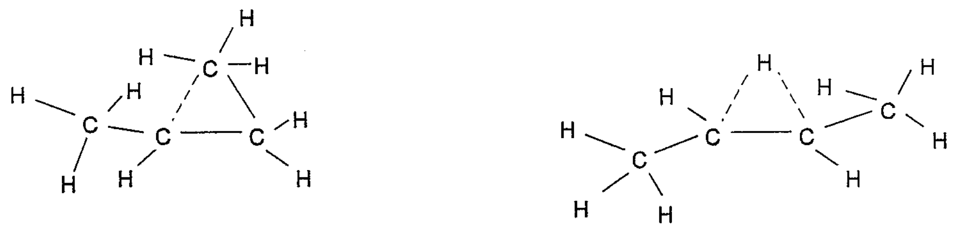


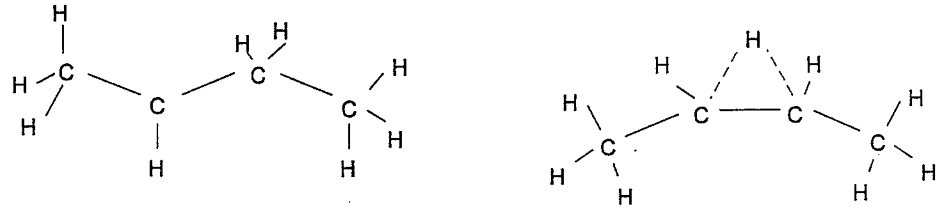
Figure 2.14 : Cation based mechanism for the isomerisation of the butenes (Choudhary and Doraiswamy, 1975:235)

According to this mechanism, addition of a proton to any of the n-butenes results in the formation of the secondary butyl cation and the formation of either *cis*-2- or *trans*-2-butene. This is consistent with the results obtained by Szabo et al. (1991:81), who found that the 2-butenes appeared first when 1-butene was passed over a fluorinated alumina catalyst. The next step in this mechanism requires the re-arrangements of the secondary butyl cation to the thermodynamically unfavourable primary butyl cation. In an attempt to understand the driving force behind the re-arrangement of the cation to a less stable configuration requires an examination of the structures of the secondary butyl cation. This was done by Carneiro et al. (1990:4065), who found that it could take one of four forms. There are the methyl bridged, the *trans*- and *cis*-H-bridged and the open-form, as shown in Figure 2.15.



Methyl bridged form

Trans H-bridged form



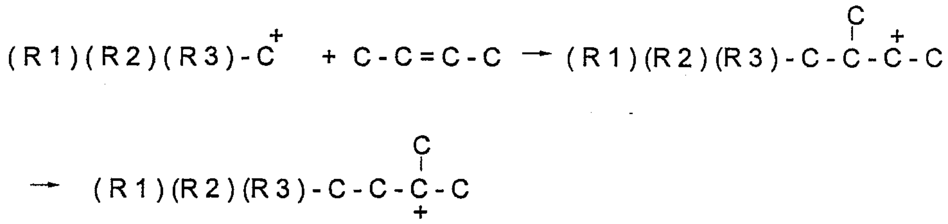
Open form

Cis H-bridged form

Figure 2.15 : Possible structure of the butyl cation (Carneiro et al., 1990:4065)

They further found that either the *trans*-H- or methyl bridged form was the most stable depending on solvent and catalyst surface properties. Assuming the methyl bridged configuration of the secondary butyl cation to be the more stable form, over fluorinated alumina, the rearrangements postulated by Choudhary (1974:39), i.e., from the secondary to the less stable primary cation may be understood.

To overcome the difficult and thermodynamically unfavourable transformation of the cyclo propane cation to the primary cation, it was proposed by Guisnet et al. (1995:1685) that the active site for the selective isomerisation of butene into isobutene on coked H-ferrierite zeolite is a cation residue $(R_1)(R_2)R_3)\text{-}C^+$. n-Butene would adsorb on this site to form a secondary cation which rearranges by methyl and hydride shifts into a tertiary cation, as shown in Figure 2.16 below.



$$(R1)(R2)(R3)\text{-}\overset{+}{C} + C\text{-}C{=}C\text{-}C \rightarrow (R1)(R2)(R3)\text{-}C\text{-}\overset{C}{\overset{|}{C}}\text{-}\overset{+}{C}\text{-}C$$

$$\rightarrow (R1)(R2)(R3)\text{-}C\text{-}C\text{-}\underset{+}{\overset{C}{\overset{|}{C}}}\text{-}C$$

Figure 2.16 : Primary butyl cation formation and rearrangement sequence (Mériaudeau et al., 1997:L1)

ß-scission of this intermediate would lead to the formation of isobutene and regeneration of the active site. According to this mechanism the isobutene reaction can only proceed via secondary-tertiary cations (Mériaudeau et al., 1997:L1).

An alternative mechanism was proposed by Mooiweer et al. (2330:1994) as shown in Figure 2.17. In an attempt to explain the low C_{5+} selectivity observed when using the zeolite Ferrierite (FER) they proposed the so called bi-molecular mechanism in combination with the shape selectivity of the zeolite Ferrierite. In this mechanism the skeletal isomerisation of an n-butene molecule starts with the donation of a proton by the acid catalyst to the olefin, under formation of a secondary cation. This species can now either isomerise or dimerise with a second butene molecule. The direct skeletal, isomerisation route can only proceed via the energetically unfavourable primary cation, and is only likely to occur when this cation is well stabilised by the catalyst. The competing dimerisation reaction leads to the formation of branched C_8 molecules, which can easily undergo skeletal isomerisation to highly branched species via secondary and tertiary cation intermediates. The formation of these highly branched dimers / oligomer was observed by them using in-situ ^{13}C MAS-NMR studies of 1-butene on FER.

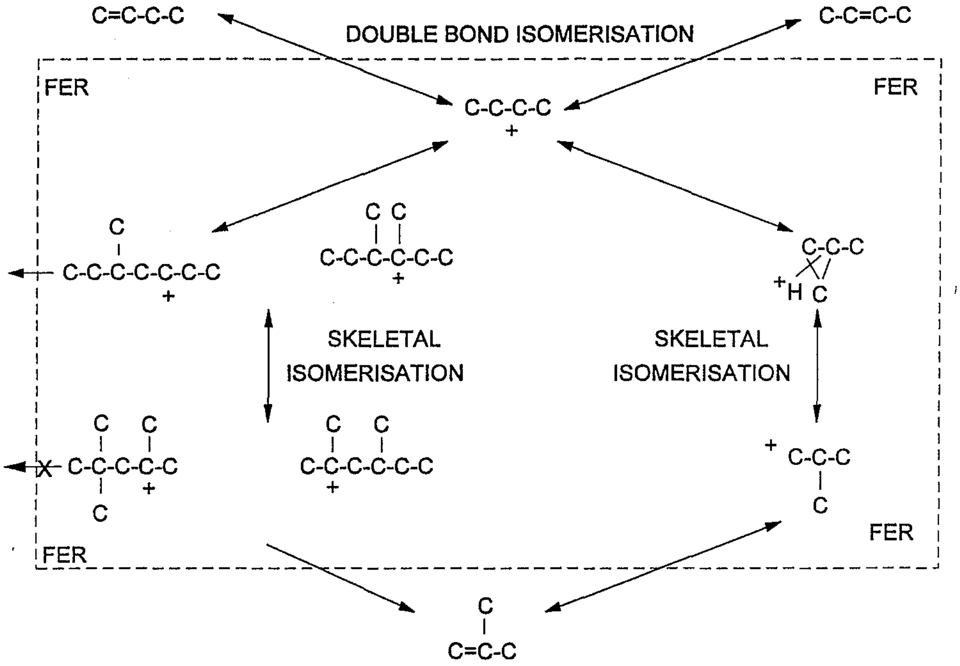


Figure 2.17 : Mechanism for the skeletal isomerisation of butenes (Mooiweer et al., 2330:1994)

Unless these highly branched molecules are cracked to n- and isobutene they lead to high C_{5+} product yield as soon as they escape from the zeolite channels. A molecular modelling study indicated that these highly branched C_8 olefins fit inside the pores of FER at the position of the intersection of the 8 and 10 membered ring channels. It was also observed that ample space is available for the skeletal isomerisation of the branched C_8 molecules inside the FER channels. Nevertheless, these highly branched C_8 olefins, in particular molecules with two methyl groups attached to a single carbon atom, are trapped in the FER channels since their transport out of these channels is strongly limited by geometric constraints. Cracking of these molecules to smaller fragments such as isobutene, is therefore greatly enhanced. The route of dimerisation of n-butene and/or isobutene, skeletal isomerisation and subsequent cracking might therefore significantly contribute to the formation of isobutene with FER. Less branched C_8 olefins are, of cause, less bulky and therefore have the ability to leave the channels more easily. ^{13}C-NMR analysis of the C_{5+} product obtained indeed indicate that these product molecules contain hardly any quaternary C atoms supporting this proposal.

The validity of the bi-molecular mechanism has been questioned. Houžvička et al. (1996:288), prepared dimers of n-butene and monitored their reactions and found that on highly acidic catalysts, which form isobutene non-selectively and show a high formation of by-products, $C_3^=$ and $C_5^=$ distributions were similar to those obtained when feeding n-butene. These and additional results presented by Houžvička et al. (1996:288) led them to conclude that the bi-molecular mechanism is mainly responsible for the formation of by-products, via the cracking of dimers of n-butene, while that the formation of isobutene runs via a monomolecular mechanism. These are the same conclusions reached by Mériaudeau et al. (1997:L1) while studying the n-butene isomerisation reaction over a H-ferrierite zeolite. They proposed that the selective isomerisation of n-butene to isobutene occurs in the channels of the H-ferrierite zeolite, where not enough space is available for the formation of the C_8 cation, and that the by-products were formed via the oligomerisation of n-butene to the iso-C_8^+ cation followed by the non-selective ß-scission of this intermediate. This non-selective isomerisation to give both n-butene, isobutene and the $C_3^=$ and $C_5^=$ by-products Mériaudeau et al. (1997:L1) concluded takes place on the external surface of the H-ferrierite zeolite as well as in the intersecting channel cavities were sufficient space for the formation of the C_8 cation exists.

2.5 SURFACE OF THE CATALYST

The material under investigation was an amorphous silica alumina. The suitability of this type of material for the n-butene skeletal isomerisation reaction, is a function of how it is prepared. It was found that aluminas, the surface of which are modified with silica, are best suited for this application. (See also Section 2.5.7 and 2.6.7). X-ray examination of this type of catalyst showed that no significant change in the physical and chemical characteristics of the starting alumina occurred during preparation (Forlani et al., 1991:243). Also, as active sites comparable to those on silica alumina are formed (Nilsen et al., 1986:342), the material will exhibit properties similar to those of alumina and silica alumina. Hence, the surface of these materials will be reviewed in this study as well as, for the sake of completeness, some of the more commonly used forms such as metal and halogen modified alumina and silica alumina.

2.5.1 ALUMINA

High purity alumina has been widely used as a support in the petro chemical industry because it is robust, porous, relatively inexpensive and is capable of contributing acidity, that can be tailored to suit the requirements of a diverse array of catalytic processes. The surface of an uncalcined alumina consists of amphoteric hydroxyl groups with low or no acidity unless they are promoted with acid enhancing impurities. To promote catalytic activity, pure alumina is activated via out gassing or calcining above 500°C, during which a complex variety of surface groups are formed. The primary change that occurs during the activation is the removal of most of the hydroxyl groups, with those that remain still being non acidic but existing in a variety of coordinated states (Peri, 1965:215). Other species that are formed include alumina cations with unsaturated co-ordination and oxygen anions (Ayame and Sawada, 1989:3055). It has generally been accepted that the outside layer of an activated alumina consists of several types of oxide ions with alumina ions forming the next lower layer (Tung and Mcininch, 1964:237). This is shown in Figure 2.18 where the grey circles represent oxide ions in the outer layer and the larger lighter circles oxide ions in the next lower layer. The small white circles represent exposed alumina ions in the same plane as the latter oxide ions. Other defects, which may occur on the surface of alumina, include anionic and cationic vacancies.

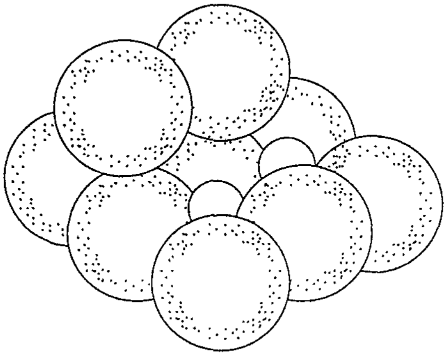


Figure 2.18 : Surface structure of alumina (Gerberich and Hall, 1966:107)

Adding water to a dehydrated alumina will result in the interaction of the water with the Lewis acid site, most probably through co-ordination with an exposed aluminum ion to form Brønsted sites. However, after co-ordination the adsorbed water molecule may ionize and the resulting hydroxyl group may locate itself in an anionic vacancy in the oxide layer while the proton drops into a cationic vacancy in the next layer. These protons, trapped in the cationic vacancies are inactive protons. They are not readily accessible to promote surface reactions unless enough energy has been furnished so that they can dissociate themselves from the cationic vacancy. Tung and Mcininch (1964:237) found that the thermal energy required to achieve this corresponds to temperatures in excess of 400°C.

The 'deactivating' effect of water on the isomerisation activity of alumina was also observed by Gerberich and Hall (1966:103). They found that as the water content of the alumina catalyst was increased, so the 1-butene bond isomerisation activity decreased. This indicates that the Lewis acid sites on the surface of the alumina react with water to form Brønsted acids which are trapped in the cationic vacancies and are thus unable to partake in the reactions. It may therefore be concluded that the bond isomerisation of 1-butene over pure alumina is catalised by Lewis acidity. Ghorbel et al. (1974:123) on the other hand, after treating the surface of alumina with a variety of poisons, concluded that the isomerisation activity arises from acid sites having oxidizing character and basic sites having reducing characters. This dual nature of the active site was also supported by Gerberich and Hall (1966:106). Thus, although the exact nature of the active site required for double bond isomerisation has not yet been established, Benesi and Winquist (1978:125) concluded that the alumina ion is the primary seat of the catalytic activity in pure alumina. Also the absence of Brønsted acidity on pure hydrated or unhydrated alumina at temperatures below 300°C, as was established by Knözinger and Kaerlein (1972:438) using infrared spectroscopy, supports this view.

2.5.2 FLUORINATED ALUMINA

The effectiveness of enhancing the skeletal isomerisation activity of alumina by fluoride addition was established by amongst others Choudhary and Doraiswamy (1971:59). Uncertainty does however still exist as to the nature of the active centres. Antipina and Chernov (1965) found, as reported by Choudhary (1977:16) that upon fluorination a new acid site was formed of comparatively low strength while the strength of the existing centres did not increase. Webb (1957:263) on the other hand found that as fluorination increased so the acid strength of the catalyst increased without the number of active centres being effected while Holm and Clark (1963:38) found that fluorination reduces the strength of the acid sites of alumina. Gerberich et al. (1966:216) suggested that a dual acid base sites, which vary in strength and number as the alumina is fluorinated, are the seats of the catalyst activity, and that residual surface hydroxyl groups act as co-catalysts. They go on to suggest that in an aqueous media the surface hydroxyl groups on the alumina exchange with fluorine as shown in Figure 2.19 below.

$$H_3O^+ + F^- + OH_s \longrightarrow 2H_2O + F_s$$

Figure 2.19 : Surface hydroxyl groups exchange with fluorine as proposed by Gerberich et al. (1966:215)

At the same time, according to Peri (1965:220) reaction of HF with the dual acid base sites of alumina should occur as in Figure 2.20. The new hydroxyl groups so formed are then replaced in accordance with Figure 2.19. Further dehydration of the surface will occur via the condensation of adjacent hydroxyl groups during pretreatment. The overall result should be a lowering of the catalyst hydrogen content.

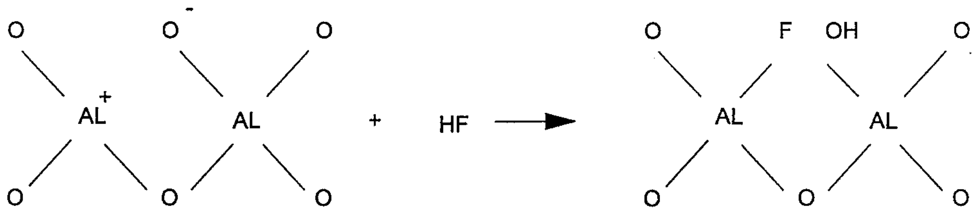


Figure 2.20 : Formation of the dual acid-base site of alumina (Gerberich et al., 1966:216)

It was found by a variety of workers that the n-butene skeletal isomerisation activity of the catalyst passed through a maximum as the fluoride content was increased, the optimum level being at ±0.86 mass % fluoride (Choudhary and Doraiswamy, 1971:59). The reason for this may be attributed to an interaction between the hydrofluoric acid and the bulk of the catalyst to form large crystallites of basic aluminum fluoride at higher loading, as observed by Webb (1957:263).

Furthermore, not all the Brønsted acid sites on the surface of the catalyst disappeared as was established by Hughes et al. (1969:58). They conclusively showed that the exposure of the dehydrated surface to water vapour resulted in an increase in the concentration of Brønsted acid sites at the expense of Lewis acid sites, i.e., that the Lewis acid sites were converted to Brønsted acid sites.

2.5.3 CHLORINATED ALUMINA

As in the case of fluoride promotion, addition of chloride to alumina enhances its activity for the skeletal isomerisation of hydrocarbons. At low chloride levels (0.1 to 1 mass %), chlorinated alumina is widely used as the acidic component of bi-functional reforming catalysts. This material exhibits a high selectivity for the skeletal isomerisation of olefin intermediates produced under reforming conditions (Sinfelt, 1964:37). The high selectivity of chlorinated alumina is attributed to its acid sites not being strong enough to crack such intermediates extensively.

Although chlorinated alumina is not strongly acidic, at low chlorine levels, an infrared study by Tanaka and Ogasawara (1970:162) showed that chemisorption of HCl on gamma alumina does form Brønsted acid sites as well as non-acidic OH groups. This contradicts the conclusions of Ayame and Sawada (1989:3055) who, also using infrared spectroscopy found that Brønsted acid and strong basic sites were not present on the surface of chlorine treated alumina. They concluded that chlorinated alumina is a solid Lewis super acid. Alumina containing as much as 15 mass % chloride have been prepared and found to be more active for both skeletal isomerisation and cracking of hydrocarbons than the promoted aluminas discussed earlier. Though surface acidity measurements of these highly chlorinated aluminas have not been done, their activity for paraffin isomerisation suggests that these materials contain Brønsted acid sites having acid strength approaching those of Friedel Crafts catalysts such as HF/SbF5 and HCl/$AlCl_3$ (Benesi and Winquist, 1978:127).

2.5.4 ALUMINAS AND BINARY OXIDES

The acidity of alumina catalysts can also be altered by the addition of a variety of anions as well as by combinations of alumina with other metal oxides. Walvekar and Halgeri (1973:387) examined the effect of a variety of metal oxides supported on alumina on the acid strength using Hammett indicators. They found, as reported by Benesi and Winquist (1978:130) that the acid strength of the binary oxides decreased in the order shown in Figure 2.21, and that only those having an acid strength equal to or greater than that corresponding to an H_o of -3 were catalytically active.

$$MoO_3 / Al_2O_3 > WO_3 / Al_2O_3 > MgO / Al_2O_3 > BeO / Al_2O_3 > ThO_3 / Al_2O_3$$

Figure 2.21 : Acid strength of various oxides on alumina (Benesi and Winquist, 1978:30)

Kania and Jurczyk (1987:5) also examined the surface acidity of gamma-alumina modified by means of co-precipitation with Fe_2O_3, Cr_2O_3, NiO, MoO_3 and MgO. They found that in all cases a reduction in the number of strongest acid sites and the formation of centres of moderate acid strength occurred. The acidity of a variety of binary metal oxides, which were prepared via the co-precipitation of the constituents at a 1:1 mole ratio, were also determined by Shibata et al. (1973:2985). In each oxide system a fairly good correlation was obtained by them between the acid strengths observed and the average electro-negativities of the two metal ions. The sequence of the acidity of the binary oxides in decreasing order, as determined by Shibata et al. (1973:2985), is shown in Figure 2.22.

$$TiO_2 / SiO_2 > TiO_2 / Al_2O_3 > ZrO_2 / Al_2O_3 > TiO_2 / CdO > TiO_2 / SnO_2 > ZnO / SiO_2$$

Figure 2.22 : Acid strength of various binary oxides (Shibata et al., 1973:2985)

2.5.5 SILICA ALUMINA

It became apparent while reviewing the literature that the suitability of silica alumina for the skeletal isomerisation of 1-butene to isobutene is a function of the way in which the material was prepared. The pretreatment and methods of preparation and the effect of this on the structure of the substrate and nature of the acid sites, that will be reviewed, are the classical co-precipitation method, referred to as silica-in-alumina and the modification of alumina with an organic silica compound called silica-on-alumina. It is the latter route that yields a catalyst better suited for the reaction being studied.

2.5.6 SILICA-IN-ALUMINA

Silica alumina catalysts are traditionally manufactured by precipitating alumina using an aluminum salt such as aluminum nitrate, in the presence of an excess of silica hydrogel. The precipitate is caused to form by addition of ammonium hydroxide while maintaining a slightly acidic slurry (Choudhary and Doraiswamy, 1971:56). The precipitate is then thoroughly washed and calcined in air at approximately 527°C to decompose the ammonium ions present in the catalyst, liberating ammonia and a proton. The latter takes the charge balancing role of the ammonium ion. However at the high temperatures used during calcination the proton can interact with the surface hydroxyl groups resulting in the loss of water (Tamele, 1950:8).

Catalyst prepared in this manner characteristically containing approximately 10 mass % alumina. Although the surface of the resulting acidic catalyst has been studied more extensively than that of any other amorphous solid (Benesi and Winquist, 1978:131) the exact nature of the acid

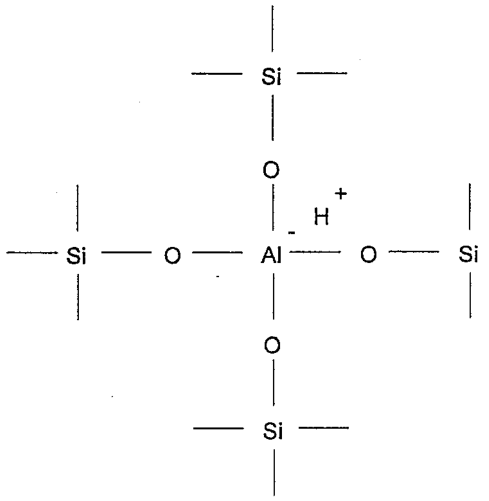


Figure 2.23 : Acid site structure on silica alumina (Thomas, 1949:2564)

site has not been established. It is however, generally accepted that the acidity is due to the interaction of silica and alumina atoms during the precipitation, i.e., as a result of isomorphous substitution of trivalent aluminum for tetravalent silicon in the silica lattice. The resultant acid sites were considered by Thomas (1949:2564) to take the form shown in Figure 2.23, with the acidity arising from the charge balancing proton remaining in the lattice.

An alternative structure of the acid site was proposed by Tamele (1950:270) and is shown in Figure 2.24. The resultant site is a Lewis acid site based on the fact that the alumina ion will fill its p-orbital by accepting an electron pair. The interaction between the aluminum, silicon and highly electrophilic oxygen atoms results in an increase in the strength of the Lewis acid site.

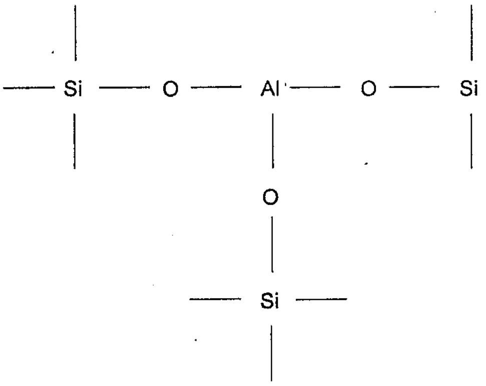


Figure 2.24 : Alternative structure of the acid site (Tamele,1950:270)

These Lewis acid sites can easily be converted to Brønsted acid by the donation of a lone pair of electrons from the oxygen atom in the water molecule. This results in the hydroxide ion being stabilized, resulting in the heterolytic cleavage of the water with the remaining proton weakly held by columbic forces. The structure of the resultant Brønsted acid site is shown in Figure 2.25.

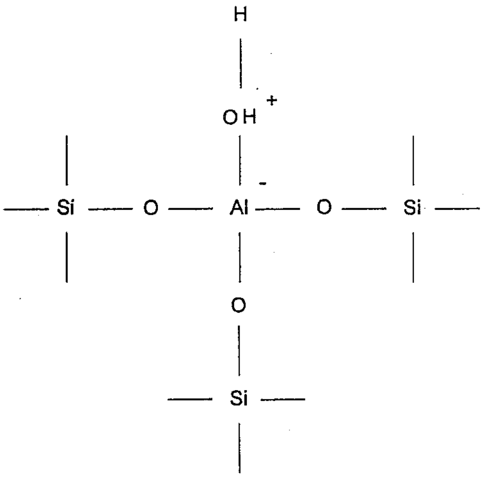


Figure 2.25 : Acid site structure in the presence of water (Hughes et al., 1969:64)

Alternatively, Plank (1947:564) suggested that aluminum is octahedral co-ordinated as shown in Figure 2.26. Here iso-morphous aluminum for silicon substitution has occurred and the alumina exists as a terminal group. It was further proposed by Hansford (1947:17) that in this configuration the protons of the coordinated water molecules would be labile and thus form a Brønsted acid.

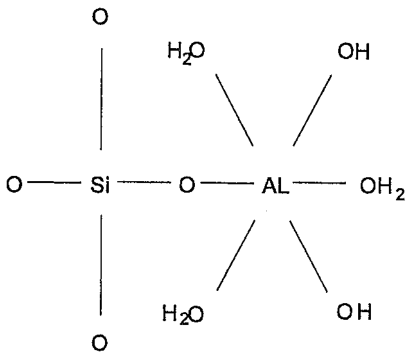


Figure 2.26 : Structure of silica alumina (Plank, 1947:564)

Using X-ray fluorescence, Leonard et al. (1964:2615) reported on the structural defects in silica alumina. These structural defects are caused by the tetrahedral coordination of the aluminum ion to oxygen ions or by either the silicon or aluminum cation being in a perturbed tetrahedral arrangement. They go on to postulate that in silica alumina the tetrahedral coordination of the aluminum ion constitute the Brønsted acid site, over the entire composition range from 0 to 100 mass % Al_2O_3. Also, a new source of Lewis acidity, sites formed by the perturbed tetrahedral arrangement of the silicon cation, becomes available at alumina loadings greater than 50 mass %. Shown in Figure 2.27 are the various structures of silica alumina pro-posed by Leonard et al. (1964:2613).

The transition from the pure tetrahedral form, Structure A, to that with alumina having a six fold coordination number, Structure C, was found to occur at around 30 mass % alumina. As expected the constitutional water content of the material also increased at this point. Dehydroxylation of silica alumina with high alumina content results in the transformation of Structure C to Structure D. This transformation occurs progressively with increasing temperature or water loss and is completed at temperatures below 470°C. Thus, dehydroxylation of high alumina content material regenerates 4 co-ordinated alumina but of a different structure than that shown previously in Figure 2-23.

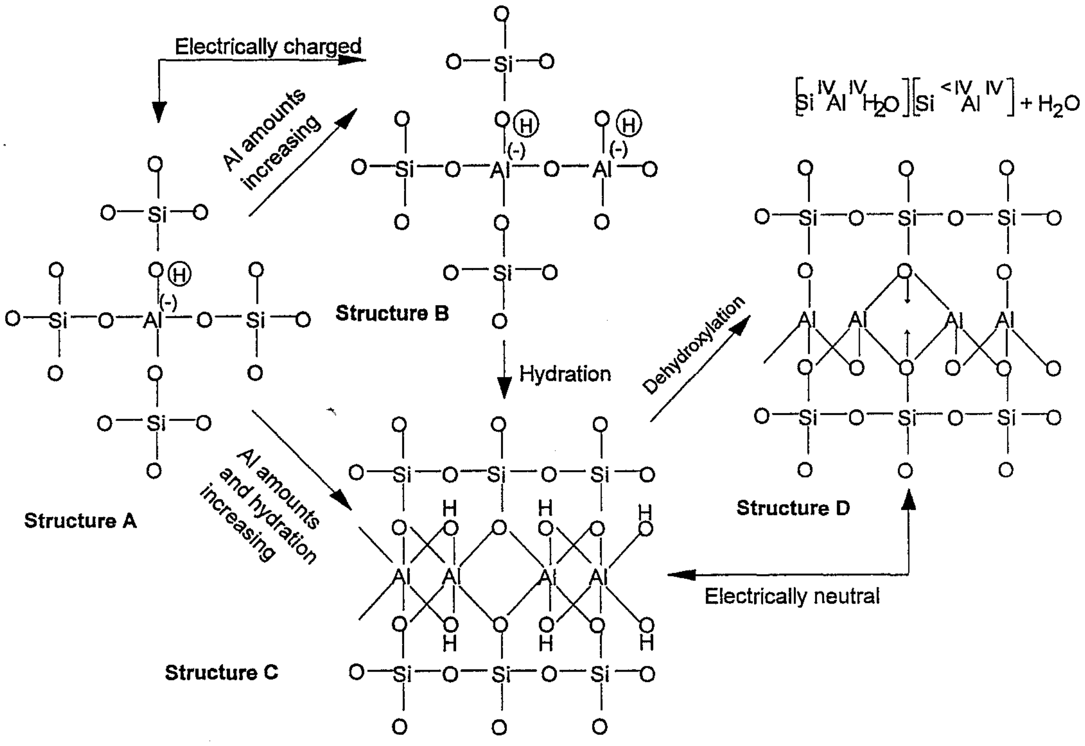


Figure 2.27 : Structural relationship in silica alumina (Leonard et al., 1964:2613)

2.5.7 SILICA - ON - ALUMINA

An alternative method to prepare a material similar to silica alumina was proposed in a set of patents by Buonomo et al. (1977:1) and Manara et al. (1977:1). This involved the reaction of tetraethoxysilane, $Si(C_2H_5)_4$, with the surface of calcined alumina followed by the hydrolysis of the new surface groups thus forming Si-OH groups similar to those on SiO_2. This type of material was found to be a strongly acidic solid and a stable, selective and highly active catalyst for the skeletal isomerisation of butene (Nilsen et al., 1986:338, Hsing, 1984:1). An added advantage of these materials is that they are not corrosive as opposed to the halogenated materials such as fluorinated or chlorinated alumina, which readily loses HF or HCl. Nilsen et al. (1986:343) proposed that a condensation reaction occurred between the tetraethoxysilane and surface hydroxyl groups present on alumina. In this way a number of species could be formed as shown in Figure 2.28 and Figure 2.29.

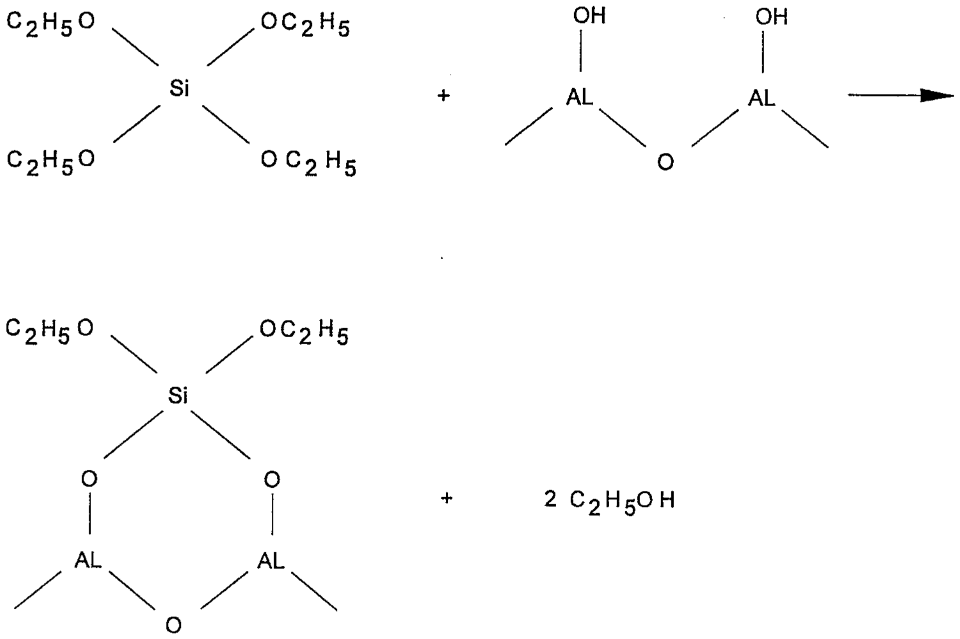


Figure 2.28 : Structure of surface groups formed during the reaction of $Si(OC_2H_5)_4$ and adjacent hydroxyl groups on Al_2O_3 (Nilsen et al., 1986:343)

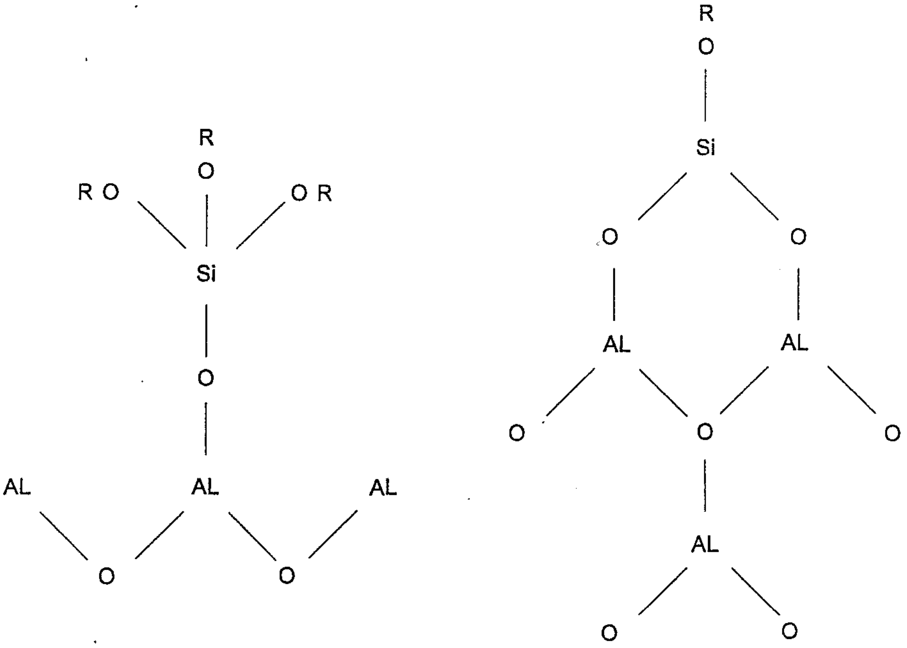


Figure 2.29 : Structure of possible surface groups on silica on alumina (Nilsen et al., 1986:343)

Hydrolysis of these groups is expected according to Nilsen et al. (1986:343) to result in the formation of silica hydroxyl groups and ethanol. Nilsen et al. (1986:343) further proposed that not all the hydroxyl groups on the surface of the alumina are converted and that regions of un-functionalised surface remain. They further proposed that the Lewis acid sites present on alumina are the exposed, co-ordinatively unsaturated Al^{+3} ions and the Brønsted acid sites the Si-OH groups. The strongest and most active Brønsted acid groups would be those positioned next to a Lewis acid site and have the structure as shown in Figure 2.30. A dual site mechanism is thus responsible for the activity of these materials (Nilsen et al., 1986:343).

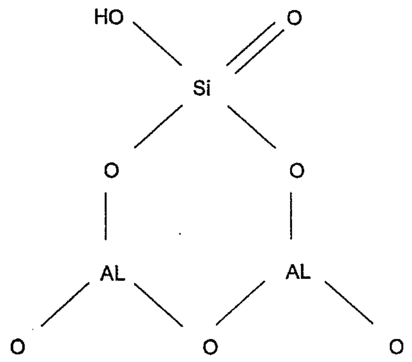


Figure 2.30 : Structure of the Brønsted site (Nilsen et al., 1986:343)

It must also be possible for the tetraethoxysilane to react with Lewis acid sites. This was the conclusion reached by Nilsen et al. (1986:343) after they found that the density of silica groups on the surface did not decrease with increasing calcination temperature, i.e., decreasing hydroxyl group concentration of the alumina prior to impregnation. One possible interaction is shown in Figure 2.31. Similar reactions can be postulated for other surface groups, but in all cases the structure of the surface, after hydrolysis, would be similar to that of silica alumina.

2.6 OTHER CATALYST SYSTEMS

2.6.1 NONE CATALYTIC ISOMERISATION

The none catalytic, i.e. thermal isomerisation of 1-butene to 2-butene, at temperatures between 500°C and 700°C was attempted by Hurd and Goldsby, (1934:1812). They found that this reaction could not be achieved without extensive decomposition of the butenes

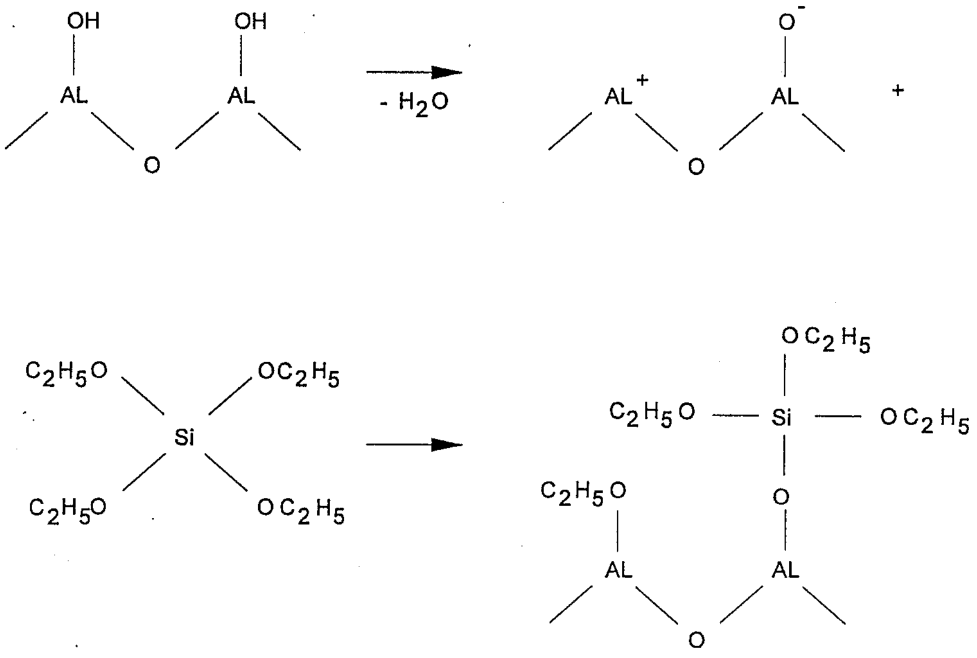


Figure 2.31 : Interaction of tetra ethoxy siliane with a Lewis acid site (Nilsen et al., 1986:343)

occurring. The *cis-trans* isomerisation of the 2-butenes may, however, be achieved without the aid of a catalyst or the formation of the decomposition products at a temperature between 345°C and 420°C, as was found by Kistiakowsky and Smith (1936:766). However, both reactions can readily be achieved with the aid of a variety of catalysts at temperatures ranging from ambient to 550°C (Condon, 1958:100).

2.6.2 ALUMINA

Alumina can undergo phase changes as a function of temperature as shown in Figure 2.32 (Stiles, 1987:18). This sensitivity of the phase to temperature should be kept in mind during the subsequent discussion.

One of the earlier references on the use of alumina for the skeletal isomerisation of butenes is that of Frost et al. (1936:374). The alumina used by them was prepared via precipitation from an aluminum sulphate solution under the action of ammonia followed by drying at 280°C to 300°C for 18 to 20 hrs in an attempt to remove the SO_4^{-2} groups.

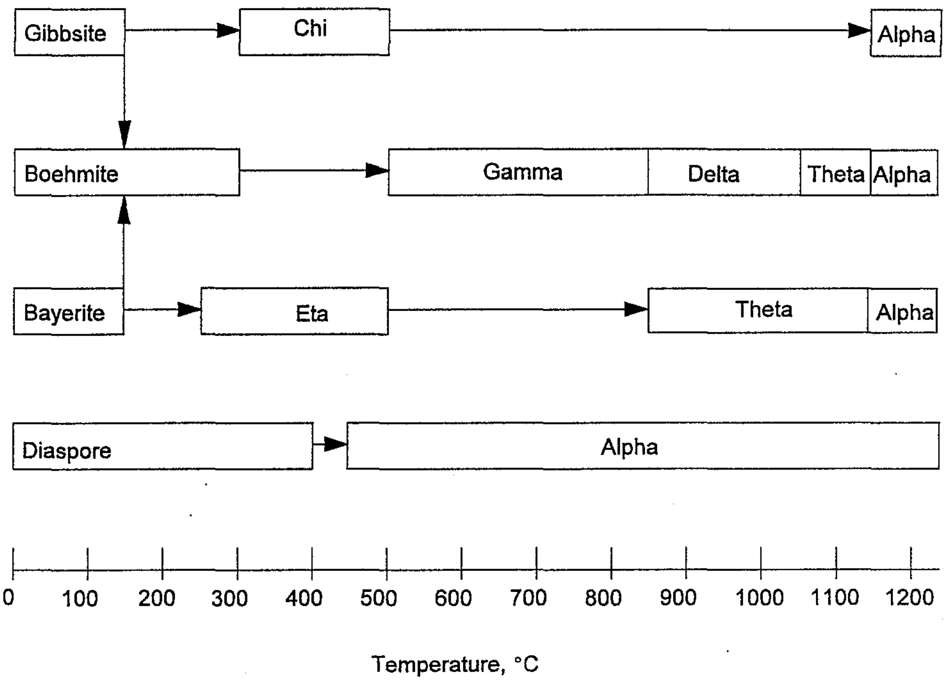


Figure 2.32 : Phase transition sequence of alumina hydroxide. Enclosed areas indicate ranges of occurrence and open areas indicate ranges of transition (Stiles, 1987:18)

Hydrocarbon vapours, together with steam to suppress polymerization at a mole ratio of 2 to 1 were passed over the catalyst at 300°C and a contact time of 116 seconds. Operating at these conditions Frost et al. (1936:374) found that the catalyst was not suitable for the skeletal isomerisation as the product contained a meagre 0.8 mass % isobutene, while 18 % of the feed was oligomerised.

Tung and Mcininch (1964:235) were more successful. Using a mixture of eta and gamma alumina, as well as amorphous material they found that the purest grade of alumina gave the best results. Operating at a temperature of 470°C and using 0.8 g of catalyst and feeding a mixture of 30 % butene in helium at a rate of 12 $ml \cdot min^{-1}$, they obtained an isobutene yield of 26,1 mole %. They further noted that the catalyst was very sensitive to impurities, in particular alkali material and the calcination temperature.

The effect of the calcination temperature was also examined by Myers (1966:95). In his study the eta-alumina catalyst was heated in a stream of hydrogen for 16 hours at temperatures ranging from 370°C to 650°C, before being rehydrated. Operating at a temperature of 371°C and a butene WHSV of 0.185 hr^{-1} and co-feeding hydrogen at a mole ration of 10:1, Myers (1966:96) found that as the water content of the catalyst was increased and the pre-treatment temperature decreased so the isomerisation rate increased. The optimum combination of drying temperature and water content, to ensure the highest isomerisation rate was found by him to be a temperature of 590°C and a water content of 1.43 mass %. The water content of the catalyst was adjusted by drying the material at 595°C for 16 hrs and rehydrating at 370°C.

Nilsen et al. (1986:342) also examined the relationship between the pretreatment temperature of alpha alumina, prior to further modification with silica, and the isomerisation rate of the final catalyst. Although the phase of the alumina did not change, a strong relationship was found with the optimum temperature being 380°C.

Alumina was also amongst the catalyst examined by Choudhary and Doraiswamy (1971:56). The catalyst was precipitated from a solution of aluminum nitrate under the action of ammonium hydroxide followed by washing, filtering and drying. They found that at 400°C and using a WHSV of 1.4 hr^{-1}, that 4.1 mass % of the 1-butene fed was converted to isobutene and that the catalyst deactivated rapidly, a lifetime of less than 1 hour, with no recovery of activity possible upon regeneration. Similar results were obtained by Stöker et al. (1986:201) who operating at 475°C and a WHSV of 2 hr^{-1} recorded a lifetime of 6 hours and an isobutene yield of only 2.5 mass %.

Amongst the more esoteric alumina type catalytic systems is that of Hönicke (1982:204). Using a catalyst prepared by the anodic oxidation of alumina as well as alpha and gamma alumina he found that in all cases the composition of the products approached the equilibrium composition with respect to 1- and 2-butenes but no evidence of skeletal isomerisation activity was observed. This is not surprising as the system was operated at a gas hourly space velocity of 6000 hr^{-1} and temperatures between 100°C and 300°C.

Finally the suitability of a gamma ray irradiated alumina for bond and skeletal isomerisation was examined by Ilie et al. (1985:4). Operating their system at a temperature of 230°C and exposing the catalyst to gamma radiation, using a ^{60}Co source, they recorded a 10 percentage point increase in the 2-butene yield compared to that obtained when using an unradiated sample. Again, as expected due to the low temperature used, isobutene was not observed in the product gases.

2.6.3 FLUORINE PROMOTED ALUMINA

Halogenated alumina can be prepared in a number of ways, the most common being impregnation, ion exchange or a vapour phase method. When a porous solid comes into contact with a liquid, capillary forces of several hundred atmospheres draw the liquid into the pores. The active component may then interact with the walls of the pore, in which case the method of preparation is described as adsorption from solution. Here the volume of solution used will be larger than the pore volume of the support. In other preparation methods where adsorption is small, the catalyst is produced by drying out of the support wetted with a solution of the active component, and the term impregnation is used. At higher loadings, greater than 5 % these methods do not lead to uniform distributions (Maatman and Prater, 1957:253). An alternative procedure to produce catalysts containing low amounts of halogens, up to 1.5 mass % in a reproducible manner is that of Turner and McGrath (1965:1). Here the support is first hydrated, than partially dehydrated and treated with a vapour of the active compound in a temperature range of 200°C to 350°C. In this method the quantity of fluorine is controlled by the duration and temperature used during the treatment. One of the earlier references of the suitability of fluorinated alumina for the skeletal isomerisation is that of Oblad and Messenger (1949:1). Using eta-alumina impregnated with between 0.5 and 10 mass % fluorine, they recorded a 60 % conversion of 1-pentene to branched pentenes with less than 10 % of the feed being lost as a result of side reactions. Although not substantiated by means of example, they go on to postulate that this catalyst would be suitable for butene skeletal isomerisation as well.

A similar conclusion was reached by Choudhary and Doraiswamy (1971:54). In an attempt to identify the most suitable catalyst for butene skeletal isomerisation they studied 46 different catalysts using a group screening technique. In this technique the suitability of the catalysts were tested in groups, i.e., instead of a single catalyst being charged to the reactor an equal quantity of a number of catalysts with similar chemical properties were used. It was assumed that the catalysts in a group did not interact and that the presence of any catalyst added to but never subtracted from the overall conversion. The catalyst from the groups that gave the most promising results were then tested individually.

Operating their system at 400°C, atmospheric pressure and a WHSV of 1.4 hr^{-1}, Choudhary and Doraiswamy (1971:59) found that an eta-alumina catalyst impregnated with 1 mass % fluorine, using ammonium fluoride as precursor, gave the best results. An initial conversion of 33.5 mass % with a half life of $t_{1/2}$ = 62.5 hours was recorded and the catalyst regaining full activity after regeneration in air at 480°C. The activation of the catalyst included the calcination of the support at 650°C in air, followed by impregnation and recalcining at 450°C.

In an attempt to suppress the deactivation observed by Choudhary and Doraiswamy (1971:59), Gerhard et al. (1980:3) proposed that the reaction be conducted in the presence of between 0.5 and 150 mass % water relative to the butenes. To replace the fluorine that would be leached out of the catalyst by the water, they go on to suggest that the water contain 40 ppm of fluorine in the form of HF. Operating their system at 450°C, a LHSV of 1.3 hr^{-1}, co-feeding 30 mole % water relative to the n-butenes and using a eta-alumina catalyst containing 0.7 mass % fluorine, Gerhard et al. (1980:13) recorded a decrease in the conversion from 51 % to 38.9 % over the 30 hours on-line period. The catalyst was previously prepared by impregnation and calcination between 400°C and 500°C. Full recovery in the initial performance of the catalyst was possible after regeneration. Also, the performance of the catalyst did not deteriorate with respect to the initial activity or the lifetime after 12 on-line and regeneration cycles (Gerhard et al., 1980:14).

An alternative to co-feeding water during the on line period in an attempt to increase the half life of the catalyst is to pretreat the material with benzene. Using a catalyst which after a pretreatment of 16 hours at 470°C contained 1 mass % fluorine and 17.6 μmole benzene per gram of alumina the skeletal isomerisation activity of such a material was examined by Davidson (1966:6). Operating at 450°C, a LHSV of 1500 /hr and a hydrogen to butene ratio of 2:1 he found that the half life of the catalyst was 69 hours and the isobutene productivity 36.1 g isobutene per ml of catalyst. He further found that using nitrogen instead of hydrogen reduced the half life to 30 hours and the productivity of isobutene to 18.5 g per ml of catalyst.

Nitrogen was also used in a Belgian patent as described by Choudhary and Doraiswamy (1974:37). In this case 2-butene was passed over a fluorinated alumina catalyst containing 0.89 mass % fluorine at 450°C and a LHSV of 1000 hr^{-1} along with nitrogen at a LHSV of 500 /hr giving an isobutene yield of 33.6 %. It was further found by them that catalysts with less than 0.5 mass % fluorine have very short lifetimes while those with fluorine content greater than 1.5 mass % gave more oligomerised and cracked products.

The effect of the operating parameters in particular temperature, butene partial pressure and contact time on the activity of fluorinated alumina was examined by Szabo et al. (1991:86). The catalyst used was gamma alumina impregnated using ammonium fluoride to a fluorine level of 4.5 mass % and calcined at 500°C. Using a fresh charge of catalyst in each experiment, Szabo et al. (1991:86) found that the optimum temperature lay between 400°C and 450°C. At lower temperatures the isomerisation rate was found to be too slow while at higher temperatures by-product formation increased. They further found that reducing the 1-butene partial pressure resulted in a decrease in the rate of side reactions, particularly the formation of C_3's and C_5's. This in turn resulted in an increase in the isobutene selectivity and as coke precursor production was suppressed, catalyst life.

Increasing the space time Szabo et al. (1991:88) found that the isobutene selectivity went through a broad maximum of approximately 31 % at a space time of 30 minutes. They further postulated that as the selectivity to by-products increased continuously the isobutene selectivity would decline at higher space times.

2.6.4 CHLORINE PROMOTED ALUMINA

Chlorination of alumina was found to have a beneficial effect on the isomerisation activity of the material. Myers (1966:98) found that adding 0.14 mass % anhydrous hydrogen chloride at 370°C to eta alumina, previously calcined at 450 °C, resulted in a three fold increase in the isomerisation rate compared to unmodified alumina. A more detailed study of the pore volume distribution and particle size on the activity of chlorinated alumina was conducted by Adams et al. (1982a:5). They found that for the catalyst to be effective the particles had to be between 0.5 x 10^{-3} cm and 160 x 10^{-3}cm with at least 10 % of the pore volume being attributed to pores having radii between 100 and 1000 Angstroms. A catalyst that met these criteria was activated at 475°C by passing nitrogen containing 0.5 volume % methyl chloride over it for 20 minutes. Using a feed that contained 20 mole % butane, 74 mole % butene and 300 ppm methyl chloride, the balance being nitrogen and operating at a WHSV of between 9 and 10.6 hr^{-1} at a temperature of 475°C, Adams et al. (1982a:12) recorded an average conversion of 37 % and selectivity of 94.4 % over the 45 hour on-line period. In a further refinement of their proposal, Adams et al. (1982b:1) specified that between 3 to 9 % of the pore volume was to be attributed to pores having radii from 100 to 10000 Angstroms, all else being as before.

2.6.5 MODIFIED ALUMINA - GENERAL

The catalytic activity of alumina modified with a number of transition metal oxides has been examined by a variety of workers.

Choudhary and Doraiswamy (1971:57) investigated the effect of preparing eta-alumina catalysts containing between 0.5 and 20 mass % chromium, platinum, lead, molybdenum, magnesium and iron. Operating at 400 °C and a WHSV of 1.4 hr^{-1} they concluded that none of the catalysts were suitable for skeletal isomerisation.

Müller (1982:3) on the other hand, was more successful. The catalyst used was prepared using alumina hydroxide treated with an excess of a ammonium salt followed by filtration, drying between 60°C and 200°C and calcination between 400°C and 800°C before being treated with BF_3, SbF_3, $BiOCl_3$ or $ZrOCl_3$. Using a catalyst containing 9.1 mass % of acidic $ZrOCl_2$ and operating at a temperature of 480°C, a GHSV of 1500 hr^{-1} and a hydrogen to n-butene ratio of 1:1, a steady conversion of 47.1 mass % and selectivity of 60.6 mass % over a 72 hours on-line period was recorded. Similar results were obtained for the other catalyst systems proposed by Müller (1982:22).

The isomerisation activity of a gamma alumina catalyst impregnated with titanium or magnesium oxides was examined by Yori et al. (1988:9). Catalysts containing up to 20.6 mass % magnesium and 36.6 mass % titanium were used in their investigation. Operating their equipment at temperatures ranging from 100°C to 300°C they found limited bond and no evidence of skeletal isomerisation activity. This is not surprising as neither magnesium or titanium oxide are acidic. The suitability of gamma alumina, converted to alpha alumina by heating to 1200°C for 30 minutes and impregnated with 6 mass % tungsten was examined by Baker and Clark (1987:484). Operating their system at a temperature of 360°C and using hydrogen and water at a ratio of 40:1, as a carrier gas, they recorded a steady isobutene yield of 36.1 mass % over their 75 minute on-line period. They further found that the activity of the catalyst was sensitive to the pretreatment procedure, in particular the gases used.

2.6.6 SILICA - IN - ALUMINA

It has long been known that Silica Alumina is capable of catalising positive ion or acid type reactions such as polymerization, alkylation, cracking and isomerisation (Clark, 1953:1477).

One of the first studies specifically of the suitability of silica alumina for butene skeletal isomerisation was conducted by Egloff et al. (1939:3571). Using a catalyst of undisclosed silica to alumina ratio, they investigated the effect of the operating temperature between 385°C to 660°C at a gas hourly space velocity of 200 hr^{-1} to 230 hr^{-1}, on the isomerisation rate. They found that at the gas hourly space velocity used, the isomerisation rate was independent of the operating temperature, the product containing 24.1 ± 1.5 % isobutene in all cases. To explain this independence of the isobutene yield with the operating temperature, they proposed that a pseudo-equilibrium was attained. That true equilibrium was not reached was established by calculating the theoretical isobutene to n-butene ratio and comparing it with that obtained. Egloff et al. (1939:3571) further found that raising the space velocity at a fixed temperature of 600°C resulted in an increase in the isobutene yield, as side reactions particularly cracking and polymerization, were suppressed.

Tung and Mcininch (1964:235) also studied the skeletal isomerisation activity of a number of catalysts including a commercially available silica alumina (Aerocat) containing 13 mass % alumina. Prior to use, the catalyst was calcined, ex-situ at 650°C for 4 hours followed by an in-situ period of 1 hour at 550°C, under helium. Using a mixture of 30 % 1-butene in helium at a total feed rate of 12 $ml{\cdot}min^{-1}$ and 0.8 g of catalyst and operating their system at 470°C, they recorded an isobutene yield of 20.8 mass % after 50 minutes on-line. No mention of lifetime or regenerateability of the catalyst was made by them. It was further found by Tung and Mcininch (1964:233) that a minimum temperature was required before the catalyst exhibited activity with bond isomerisation reaching equilibrium at 200°C and skeletal isomerisation first being observed at 310°C. Similarly the isomerisation activity over Houdry M-46 silica alumina was examined by Gerberich and Hall (1966:103). In the case of their work, however, the reaction temperature was held below 150°C at all times. Consequently, as expected in accordance with the work done by Tung and Mcininch (1964:233) only bond, i.e., no skeletal isomerisation was observed.

Silica Alumina was also considered by Choudhary and Doraiswamy (1971:56) during their search for a suitable skeletal isomerisation catalyst. Using a group screening technique as discussed previously, they loaded silica alumina (Davidson grade) together with equal quantities of four fluorine modified silica aluminas, fluorine content ranging from 0.5 to 2 mass % into an integral reactor. Operating their system at 400°C and a WHSV of 1.44 hr^{-1} they recorded a conversion to isobutene of 8 % and a selectivity of 67.5 %. However, no further work using the members of this group was done by Choudhary and Doraiswamy (1971:59). A similar result was obtained by Nilsen et al. (1986:341) at 500°C and found that the material exhibited limited skeletal isomerisation activity.

Finally, the activity of the class of aluminum silicates including various fuller's earth and clays such as montmorillonite, and artificially prepared materials such as Tonsil for use in the skeletal isomerisation of n-butene was also studied by Ipatieff and Schaad (1939:1). Using a catalyst of undisclosed silica to alumina ratio, and calcining the Tonsil clay at 315 to 540 °C for an optimum time of 16 hours before use, they examined the activity and isobutene selectivity at temperatures between 350°C to 500°C and gas hourly space velocities of 235 hr^{-1} to 500 hr^{-1}. They found that as the temperature was increased, so the isobutene yield increased. They further found that increasing the space velocities above 470 hr^{-1} resulted in a dramatic decrease in the polymerization selectivity. Alternatively the polymerization selectivity could also be suppressed by using a diluent such as butane, i.e., by reducing the butene partial pressure. Cracking activity was also observed particularly when operating the system at high temperatures and low space velocities, i.e., extended residence times. To determine the long-term stability of the catalyst a lifetime study lasting 94 hours at a temperature of 450°C using a space velocity of approximately 210 hr^{-1} to 240 hr^{-1} was conducted. Over this period the isobutene yield dropped form an initial value of 24.1 mole % to 19.6 mole %, i.e., a cycle lifetime, defined as the time for the yield to drop to 90 mass % of its initial value, of 50 hours. The catalyst was successfully regenerated by heating in a stream of dry air for 10 hours. During regeneration, the temperature was increased from 125°C to 480°C followed by 8 hours at 480°C.

2.6.7 SILICA MODIFIED ALUMINA

Silica modified alumina catalysts may be prepared using calcined gamma alumina before bringing it into contact with a suitable silane in either the vapour phase (Hsing, 1984:1) or liquid phase with ethanol or n-hexane as the solvent (Nilsen et al., 1986:338). The preparation of the catalyst is completed by calcining the material thereby removing the organic components. Using gamma alumina supplied by Ketjen/Akzo, Nilsen et al. (1986:342) investigated the effect of the calcination temperature of the support on the activity of the final catalyst. In their investigation the support was pretreated in helium for 18 hours at temperatures ranging from 300°C to 660°C followed by contacting the material with tetraethoxysilane using n-hexane as solvent. After evaporating the solvent the organic fraction was removed during a number of calcination and regeneration cycles. Using catalysts so prepared, containing approximately 3.5 mass % silica, they found that the rate of butene isomerisation, at a conversion level of 0.4 to 4 % was strongly dependent on the calcination temperature of the support, the optimum being a temperature of 400°C. They further found that the catalyst activity increased as the concentration of silica containing groups increased as long as the silica was restricted to a monolayer. Catalysts of this type were found by them to exceed the performance of silica - in - alumina.

An alternative production technique and investigation as to the suitability of silicated alumina, was conducted by Hsing (1984:1). Gamma alumina with a sodium content of less than 0.01 mass % was first calcined at 300°C for 8 hours before being placed in a suitable container and evacuated. Following this, liquid silane was vaporized into the vacuum chamber where it is adsorbed onto the alumina. Investigating the catalytic properties of the material, Hsing (1984:5) found that an initial isobutene yield of 35.7 mass % could be obtained. The system was operated using a water flow rate of 0.02 to 0.5 moles per mole of alkene, a LHSV of between 1 and 8 and a temperature of between 450°C and 550°C. Analysing his data further it was established that the cycle life of the catalyst, the period for the yield to drop to 90 % of the initial value, was 12 hours. The initial activity of the catalyst could be recovered by burning the carbon deposited during the on-line period. Furthermore, operating the catalyst on a 24 hours on-line cycle followed by regeneration, the material showed no signs of deactivation over a two month period.

The fact that the addition of silica, using tetraethoxysilane stabilizes gamma alumina towards thermal sintering at high temperatures, in the presence of steam was confirmed by Beguin et al. (1991:603). Operating at temperatures far above those used for skeletal isomerisation, i.e., 1050 to 1220°C, they found that the stability of the catalyst increased with increasing silica loading reaching a plateau at approximately 3 mass % silica. The silane used in this work was tetraethoxysilane with ethanol as the solvent. The carrier was not pre-treated prior to modification. Similar results were obtained by Forlani et al. (1991:244), who found that the surface area of gamma alumina decreases at temperatures above 700°C, while silicated gamma alumina does not sinter at temperatures of 1000°C.

A performance similar to that obtained by Hsing (1984:29) was also reported by Snamprogetti (Anon, 1982:4). Starting with an active alumina catalyst, the surface of which was modified with silica using an unspecified organic silica compound, they recorded an isobutene yield of 28 ± 5 mass % at a temperature of 470 ± 20°C and a WHSV of 2.5 ± 1 g/g/hr. No further detail of the catalyst or process are given.

Yori et al. (1988:3) prepared catalysts with silica contents ranging from 1.4 to 20.8 mass %, using gamma alumina that had previously been calcined at 650°C and treated with tetraethoxysilane. Using a bench reactor containing 0.135 g of catalyst and operating at temperatures between 100°C and 300°C, 1-butene and nitrogen were passed over the catalyst at a rate of 12 $\mathrm{ml \cdot min^{-1}}$ and 62 $\mathrm{ml \cdot min^{-1}}$ respectively. They found that as the silica to alumina ratio was increased, so the bond isomerisation equilibrium was reached at lower and lower temperatures. They further found that at the temperatures used only catalyst containing between 13.1 mass % and 20.8 mass % silica were capable of producing traces of the skeletal isomer, isobutene. Examining the BET surface area of the materials, Yori et al. (1988:3) found that it was not effected by silica loading up to 20.8 mass % but remained approximately constant at 190 m^2/g.

A detailed investigation of silicated alumina was also conducted by Støcker et al. (1986:201), who also examined the effect of lanthanum on the activity of the catalyst. The alumina support was calcined at 400 °C for 18 hours before it was modified using tetraethoxysilane silane. To incorporate lanthanum the silicated material was recalcined and impregnated using a lanthanum nitrate solution. Using catalysts prepared in this manner, Støcker et al. (1986:201) found that silicated aluminas, with a silica content of 2.4 mass %, and without lanthanum were good skeletal isomerisation catalysts, giving isobutene yields of 20 % when operated at 475°C and a WHSV of 2 hr^{-1}. The addition of lanthanum to silicated alumina in an attempt to neutralize the strong acid sites, was in fact found by Forlani et al. (1991:245) to encourage "reverse" bond isomerisation from the 2-butenes to 1-butene. The best catalyst for this reaction was found to be one that contained 10 mass % lanthanum and 1.5 mass % silica on gamma alumina. No further details of the reaction conditions were given.

2.7 SUMMARY

The final use of the isobutene produced is as a fuel additive, to replace lead, in the form of a tertiary ether. (Unzelman et al., 1971:47; Unzelman, 1989a:44, 1989b:33). A number of alternative processes, using a variety of raw materials for the production of isobutene are available as discussed, by among others, Muddarris and Pettman (1980:92), Logwinuk and Graig (1964:66), Vors et al., (1981:1) and Remirez, 1987:21). However, the complexity of these processes and availability of the feed stocks prevent their use at Sasol Chemical Industries. Hence the feasibility of the skeletal isomerisation of the n-butenes to isobutene was investigated. This promised to be a possible way, due to feedstock availability and a relatively simple process flow sheet, to prepare a suitable feed stock for the etherification plant.

A investigation as to the reactions that can take place during the bond and skeletal isomerisation of 1-butene, and an analysis of the reactivity of the various products during the preparation of the tertiary ether, was carried out. It was found that the by-products formed consisted mainly of the linear butene isomers, C_4 paraffins and lighter (C_3) and heavier (C_5) components (Kirk and Othmer, 1984:356, Choudhary and Doraiswamy, 1971:230, Andy et al., 1998:322). Examining the affinity of these components for reactions with an alcohol, at the conditions traditionally used for the preparation of ethers, it was found that all of these, including the linear butenes 1-butene, *cis*-2-butene and *trans*-2-butene, were inert. Hence, high yields of the desired tertiary ethers could be achieved without costly purification of the products from the isomerisation plant being required (Ancillotti and Pescarollo, 1986:1; Tejero et al., 1989:1269). An examination of the thermodynamics showed that even if the only by-products formed were *cis*- and *trans*-2-butene, the maximum yield of isobutene possible, at the optimum temperature of 520°C, is 36.6 mass % (Kilpatrick et al., 1946:559). However, as isobutene can be removed from the products via etherification, a high yield of isobutene may be achieved by recycling the gaseous products from the etherification reactor to the isomerisation reactor. The successful implementation of this closed loop system requires that the formation of the by-products other than *cis*- and *trans*-2-butene be kept as low as possible. The build-up of the lighter and heavier by-products in the recycled stream could best be prevented by venting some of the gaseous material. Unfortunately, this will also lead to the loss of valuable feed stocks and should thus be avoided. Hence, a suitable skeletal isomerisation catalyst will firstly have to exhibit a high selectivity to isobutene, and secondly a high conversion of the n-butenes per pass.

A search of the literature was conducted in the attempt to locate such a material. The results from the literature survey are given in Chapter 2. Searching the literature for details of a suitable catalyst and a kinetic equation that could be used for the rigorous design of a skeletal isomerisation reactor, it was noted that little information was available. What was found was that the law of mass action could be used to describe the rate of n-butene conversion and the formation of by-products (Choudhary and Doraiswamy, 1971:55, Bianchi et al., 1994:554, Simon et al., 1994:480, Szabo et al., 1993:319) and that silanised alumina catalysts were the most suitable for this application.

Examining the bond isomerisation mechanism over a catalyst containing predominantly Lewis acid sites, it was concluded that both an acid and base site were required, and that the rearrangement of the olefin proceeds via the hydrogen switch mechanism (Gerberich and Hall, 1966:107). It was also established that Lewis sites are not capable of catalising skeletal isomerisation and are thus not suitable for this reaction (Condon, 1958:44). In the case of Brønsted acids, it was found that the rearrangement of the olefin proceeds via the classical cation mechanism (Choudhary and Doraiswamy, 1975:253). The rearrangement of the butyl cation from the secondary to the less stable primary butyl cation, the dehydrogenation of which results in the formation of isobutene, can only be accommodated if it is assumed that the butyl cation assumes the methyl bridged configuration after formation (Carneiro et al. 1990:4065). Alternatively, a bi-molecular mechanism consisting of dimerisation, isomerisation followed by cracking to the desired products, was proposed (Mooiweer et al., 1994:2330). However, the validity of this mechanism is still being debated in the literature (Houžvička et al., 1996:288, Mériaudeau et al., 1997:L).

Examining the nature of the active sites on alumina and silica alumina, it was found that in the case of the former the required Brønsted sites were absent (Knözinger and Kaerlein, 1972:438). The required sites may be created either by halogenating alumina with fluorine

(Holm and Clark, 1963:38; Gerberich et al., 1966:216) or chlorine (Tanaka and Ogasawara, 1970:162; Ayame and Sawada, 1989:3055) or by silanising the material with tetra-ethoxysilane (Buonomo et al., 1977:1; Manara et al., 1977:1, Nielsen et al., 1986:338). To establish which of these materials, including silica alumina prepared in the conventional way, was suitable for use in a commercial application, the results achieved by other workers were reviewed. It was found that in most cases, the catalyst deactivated during the on-line period. However, the initial performance could usually be recovered by regenerating the material, i.e., by burning off coke that was deposited on the catalyst during the on-line period. This was reported by amongst others Choudhary and Doraiswamy (1971:56). From this it may be concluded that in a commercial plant a multi-reactor system will be required to guarantee that the composition of the products from the isomerisation reactors remains stable. A stable product stream will be required to enable the uninterrupted operation of the etherification plant and other down stream processes. It was further found that the period between regenerations could be extended by protecting the Brønsted acid sites present on the surface of the catalyst. The most effective manner in which this could be done was to co-feed water (Choudhary and Doraiswamy, 1971:59; Gerhard et al., 1980:3). The water co-fed interacted with the Lewis acid sites to form the required Brønsted acid sites (Hughes et al., 1969:58).

In the case of fluorinated or chlorinated alumina, the loss of the halogen to the water could be counteracted by spiking the water with a suitable halogen compound such as HF or HCl. The corrosive nature of these materials and their presence in the final product may be undesirable. Hence it may be concluded that the halogenated aluminas are not suitable for use in a commercial skeletal isomerisation plant.

Examining the results achieved by other workers using silica alumina for the skeletal isomerisation of the n-butenes to isobutene, it was found that the material had little to no activity (Choudhary and Doraiswamy, 1971:59; Nielsen et al., 1986:341). Silanised alumina, prepared using tetraethoxysilane was found to be a highly active material for this reaction (Hsing, 1984:1, Nilsen et al., 1986:338). It was further noted that the activity and stability of the material was largely dependent on the procedure used during the pre-treatment of the alumina support and the water to hydrocarbon ratio used during the on-line period. In addition to this, it was established that silanising alumina enhanced the resistance of the material to thermal sintering, particularly in the presence of water, making it suitable for use in a commercial process (Beguin et al., 1991:603). An attempt to locate the intrinsic kinetic equation particular to this type of catalyst, suitable for the rigorous design of the skeletal isomerisation reactor, was not successful.

However, a proprietary, experimental amorphous silica alumina catalyst, shown previously to be suitable for the n-butene skeletal isomerisation, could be obtained and was used during this study. The performance of the material was evaluated and an intrinsic kinetic equation suitable for use in the design of a commercial skeletal isomerisation reactor developed during this study.