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Catalytic skeletal isomerization of linear butenes to isobutene

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Abstract

The increased demand for isobutene, used for the production of the octane-enhancer methyl *tert*-butyl ether, has generated tremendous interest in the catalytic conversion of the linear butenes to isobutene. In this review we survey the progress made since the late 1970s in implementing the catalytic skeletal isomerization reaction of these linear alkenes. Halogenated catalysts, especially those based on alumina, and prepared using a variety of compounds of fluorine, chlorine or bromine, have been shown to exhibit both high conversions and selectivities for the reaction, resulting in high yields of isobutene, when water is added to the feed stream. Elution of the halogen from the catalyst leads to the loss of catalytic activity and necessitates the continuous or discontinuous addition of the halogen compound. As a consequence, environmental and other considerations are most likely to weigh against the industrial usage of these catalysts. Another class of catalysts exhibiting high activities and selectivities, again in the presence of water, are the silicated aluminas. No information is, however, available on their long-term stability. Even alumina on its own displays high activity and selectivity, provided water is co-fed with the hydrocarbon stream. More recent results obtained over other types of catalysts such as zeolites and molecular sieves are also presented. Most promising are the results obtained with the zeolite ferrierite which gives high yields of the branched isomer in the absence of any other additive or diluent. The catalyst also appears to be fairly stable showing no decrease in the yield of isobutene after 14 days on-stream. The high yields of isobutene can be ascribed to the small channel diameters which prevent the extensive dimerization or oligomerization of the linear butenes or of the product isobutene. Plans for the first large-scale demonstration plant to produce isobutene from *n*-butenes using ferrierite as catalyst have already been announced in the United States.

1. INTRODUCTION

The last review on the catalytic skeletal isomerization of linear butenes to isobutene appeared in 1977 [1] as a section in a review paper which dealt with the activity and surface properties of fluorinated aluminas. Since that time considerable interest has been shown in this reaction because isobutene is the alkene precursor in the synthesis of the branched fuel ethers methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). MTBE in particular

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is the octane-enhancer of choice to replace tetraethyllead in reformulated gasoline [2]. Other current industrial uses of isobutene include those as the monomer in the production of polyisobutene, as one of the monomers for butyl rubber and polybutene manufacture, and for the production of a variety of chemicals [3].

Currently for the production of MTBE, isobutene is predominantly obtained from catalytic or steam cracking fractions [4]. Since the supply of isobutene from these sources is insufficient to meet anticipated demand, alternative routes have been implemented or investigated. These include the dehydrogenation of isobutane [5], the dehydration of *tert*-butanol [6] and of isobutanol [7], which in turn can be obtained from isosynthesis [8–10], the exhaustive metathetical ethenolysis of branched alkenes [11] and the catalytic skeletal isomerization (SI) of linear butenes. In this review, we critically evaluate the progress achieved since the late 1970s in the catalytic conversion of linear butenes to isobutene as reported in both the open and patent literature. Our aim in preparing this non-exhaustive review of the literature was to identify the types or classes of compounds or materials that have been studied and used as catalysts for this reaction, to obtain an understanding of their observed catalytic activities and selectivities and to gain an appreciation of the reaction conditions required by each group of catalysts. The advantages or disadvantages presented by each group are also discussed where appropriate.

In an earlier survey [12], the kinetics and mechanism of the isomerization reaction, the thermodynamic and physical properties of the four butenes and the thermodynamics of the reaction system were reviewed. The reaction system is a rather complex one since apart from the reversible skeletal isomerization reaction, the *cis–trans* and double-bond shift reactions of the linear butenes are also occurring (see Fig. 1). In the reaction mechanism depicted in Fig. 1 the rearrangement of the carbenium ion is shown to proceed via a protonated cyclopropane ring which on opening forms the primary carbenium ion [13]. The temperature dependence of the equilibrium concentrations has also been reported [14] and the results show (see Fig. 2) that the equilibrium concentration of isobutene in the mixture of butenes decreases with increasing reaction temperature. In practice, in the catalytic conversion of linear butenes to isobutene, the yield of isobutene is further lowered due to the occurrence of side-reactions such as dimerization to C_8, transformation of this product into C_3 and C_5, hydrogen transfer and coking [15]. As a consequence, the SI reaction is conducted at low pressures which, as shown by thermodynamic calculations [15], minimize the undesirable dimerization and polymerization reactions.

The skeletal isomerization reaction has also been shown to be a more demanding reaction than both the *cis–trans* and double-bond shift isomerization reactions, since it only proceeds over sites of higher acid strength [16,17].
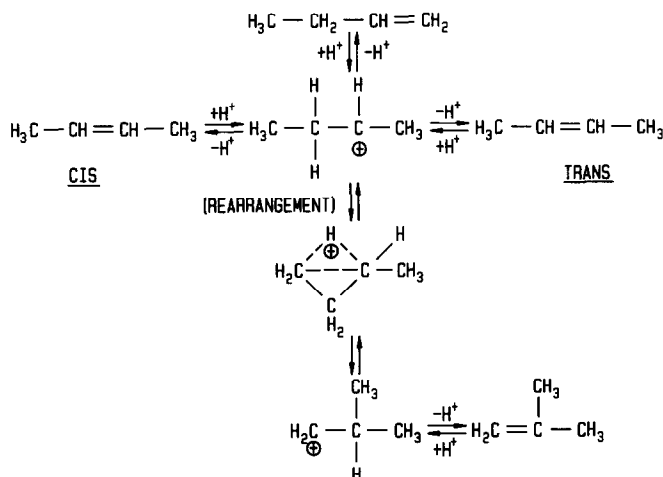
Fig. 1. Reaction scheme for the isomerization reactions of the butenes.

The results, obtained using H_R indicators, the dehydration of 4-methyl-2-pentanol as the catalytic test reaction and a variety of acid catalysts, indicated that there is a strong correlation between the occurrence of a given catalytic reaction and the presence of sites of a given acid strength (see Table 1). Similar results were subsequently obtained by these authors using a series of silica–alumina catalysts with compositions ranging from 0 to 100% Al_2O_3 [17].

A confirmation of the above results was obtained in our laboratories by carrying out some of the above-mentioned acid-catalyzed reactions, and some other reactions, over the same type of catalyst as a function of temperature [18]. Acid-catalyzed reactions have been categorized as difficult/demanding or facile from either (i) the temperature required to attain a particular reaction rate over a specific catalyst [19], or (ii) the rate at which the reaction proceeds over a catalyst at a fixed temperature [20]. These previous evaluations have shown that the cracking of alkanes (e.g. n-hexane) can be considered a difficult reaction requiring strongly acidic sites, whereas alcohol dehydration is one of the most facile acid-catalyzed reactions [21]. It has further been demonstrated that the more difficult the reaction is, the higher must be the acid strength of the sites [22,23] or the temperature [23] in order for the catalytic reaction to proceed. We have therefore examined the conversion of 1-butene to cis/trans-2-butene and to isobutene, 1- and 2-butanol dehydration to the butenes, methanol conversion to dimethyl ether, as well as n-hexane cracking as a function of the reaction temperature over the same catalyst, viz. zeolite HZSM-5. The results in Fig. 3 show that the conversion of 1-butene to cis/trans-2-butene (the most facile reaction in this group of acid-catalyzed reactions) and the alcohol dehydration reactions occur at lower temperatures than the skeletal isomerization reaction or the n-hexane cracking
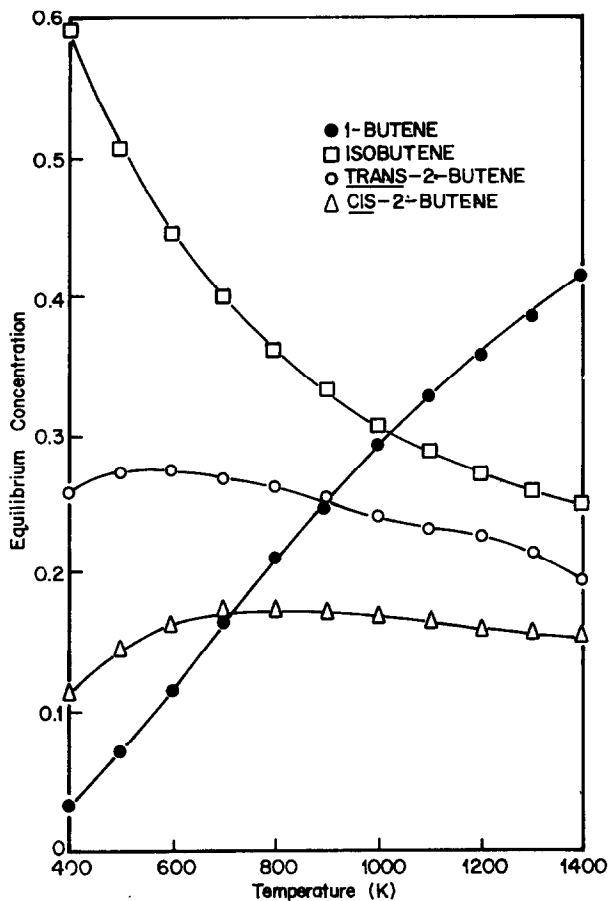
Fig. 2. Temperature dependence of the equilibrium concentrations for the isomerization reactions of the butenes [14].

TABLE 1

Correlation between the nature of the catalytic reaction and the acid strength of the catalyst [17]

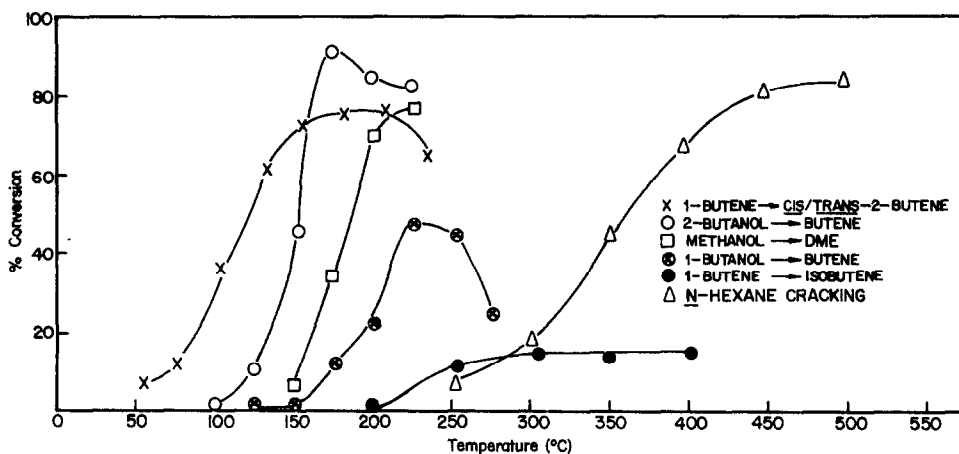| Acid strength	Dehydration	cis–trans Isomerization	Positional isomerization (1)–(2)	Positional isomerization (beyond 2-position)	Skeletal isomerization
$4.75 \geqslant H_R > 0.82$	+	–	–	–	–
$0.82 \geqslant H_R > -4.04$	+	+	+	–	–
$-4.04 \geqslant H_R > -6.63$	+	+	+	+	–
$-6.63 \geqslant H_R$	+	+	+	+	+

Fig. 3. Acid-catalyzed conversions as a function of temperature over zeolite HZSM-5 [18].

reaction (the latter being the most demanding reaction). From our results we can rank the reactions in terms of their difficulty as follows: n-hexane cracking > skeletal isomerization of linear butenes > alcohol dehydration > double-bond shift. The SI reaction can therefore be considered to be of moderate difficulty, requiring sites of relatively higher acid strength. This has been explained in terms of the skeletal isomerization reaction proceeding through the thermodynamically less stable primary butyl carbenium ion intermediate [12]. Thus, whereas η-alumina shows only low activity for the skeletal isomerization reaction, fluorinated η-aluminas are significantly more active [24]. This has been ascribed to the fact that fluorination increases the acid strength of the aluminas [1]. Chlorination of alumina also leads to the same results [25].

An earlier review [12] surveyed the catalytic systems employed prior to 1974 in carrying out the SI reaction. These included metal halide catalysts, alumina and aluminosilicate catalysts, phosphoric acid, phosphate and fluorinated alumina catalysts. From their own work as well [24], the authors concluded that fluorinated η-alumina, containing 1 wt.-% F, was the best catalyst, exhibiting the highest activity (33.5% conversion), high selectivity (87.1% for isobutene), a catalyst half-life of 61.5 hours and excellent regenerability.

Similar conclusions regarding the activity and selectivity of fluorinated catalysts for this reaction were reached in that author's 1977 review [1] in which the preparation, catalytic activity, reactivation, surface properties and active sites of these catalysts were described. In a report on the upgrading of C_4 cracking cuts with acid catalysts [3], the SI reaction of the n-butenes was also briefly reviewed.

In another review by Ghosh and Kydd [26], the preparation, structure,

TABLE 2

Tabulated summary of literature (selected results)

Catalyst type	Reaction temp. (°C)	Press. (atm)	Space velocity (g/g·h)	Feed and additives	Conversion (%)	$i\text{-}C_4^=$ (%) selectivity	Time-on stream (h)	Reference
1% F/Al_2O_3	450	1	ca. 0.5[a]	0.12% $C_3^=$, 16.24% $n\text{-}C_4$, 4.73% $i\text{-}C_4$, 10.14% $1\text{-}C_4^=$, 67.67% $2\text{-}C_4^=$, 1.10% $i\text{-}C_4^=$, $H_2O/HC=2.2/1$	40.9	89.4	–	Juguin and Miquel, 1981 (IFP)
0.7% $F/\eta\text{-}Al_2O_3$	450	1.1	ca. 0.8[a]	1-Butene, 10% H_2O, 40 ppm HF	51.0	63.8	1	Franz et al., 1983 (Huels)
					38.9	75.0	30	
$BiOCl/Al_2O_3$	480	1	ca. 3.9[a]	1-Butene, $1\text{-}C_4^=/H_2=1/1.5$	49.4[b]	66.8[b]	–	
HCl/Al_2O_3	450	1	ca. 3.8[a]	0.5% $i\text{-}C_4^=$, 76% $n\text{-}C_4^=$s, 23.5% C_4s, $Feed/H_2=1/1.5$	61.0[b]	42.0[b]	20	Müller et al., 1982 (Erdölchemie)
HCl/Al_2O_3	450	1	ca. 3.8[a]	0.5% $i\text{-}C_4^=$, 76% $n\text{-}C_4^=$s, 23.5% C_4s, $Feed/H_2=1/1.5$	58.5[b]	42.7[b]	100	
CH_3Cl/Al_2O_3	475	1.05	9.4	16.3% $n\text{-}C_4$, 4.0% $i\text{-}C_4$, 44.1% $1\text{-}C_4^=$, 17.5% trans-$2\text{-}C_4^=$, 12.0% cis-$2\text{-}C_4^=$ (in mol-%), 5.8% N_2, 300 ppm CH_3Cl	33.7	96	45.3	Adams et al., 1983 (Polysar)
20 ppm Pd, 3% SiO_2/Al_2O_3	450	1	ca. 0.5[a]	0.12% $C_3^=$, 16.24% $n\text{-}C_4$, 4.73% $i\text{-}C_4$, 10.14% $1\text{-}C_4^=$, 67.67% $2\text{-}C_4^=$, 1.10% $i\text{-}C_4^=$, $H_2O/HC=2.2/1$	40.9	90.3	–	Juguin and Miquel, 1982 and 1984 (IFP)
Al_2O_3	482	1	ca. 1.8[a]	2-Butene, 3.34% H_2O	30.9	85.1	3.0	Myers and Strope, 1984 (Phillips Petroleum)
Al_2O_3	482	1	ca. 1.2[a]	2-Butene, 11.4% H_2O	33.2	83.5	6.25	

CCl_4, 1% Pd/Al_2O_3	350	ca. 18	ca. 0.5	2-Butene, 2 000 ppm CCl_4, H_2 (4 bar)	31	64	–	
CCl_4, 1% Pd/Al_2O_3	350	ca. 13	0.5	2-Butene, H_2 (ca. 1.1. bar), 42.8% n-Butane	34.1	85	–	Eleazar et al., 1984 (Engelhard)
CCl_4, 1% Pd/Al_2O_3	350–375	ca. 26	0.5	2-Butene, H_2 (ca. 1.1 bar), 47% n-Butane	51	74	682	
Partially Na$^+$-exchanged borosilicate	525	0.5	7.6	1-Butene, H_2/ 1-C_4^- =2.0/1	36.5	66.3	–	Sikkenga, 1985 (Standard Oil)
2.7% SiO_2/Al_2O_3	475	–	2	n-Butene	49 44	72 76	1 6	Nilsen et al., 1985 (Statoil and CIIR)
6.1% SiO_2/Al_2O_3	475	–	2	n-Butene	56 49	55 70	1 6	
BPO_4 on SiO_2/Al_2O_3	475	–	2	n-Butene	43 34	79 83	1 5.5	
'Silicalite'	325	1.6	31.4	49% n-C_4^-, 49.6% n-C_4, 1.4% light HCs H_2O/feed=1.11/1	79.4	12.5	–	de Clippeleir et al., 1985 (Labofina)
0.5% La, 1.1% Si/Al_2O_3	500	–	2	1-Butene	>28.3	75	4	Stöcker et al., 1986 (CIIR)
n-BuBr/Al_2O_3	447	1	ca. 2.6[a]	1-Butene, 210 ppm n-BuBr	29.9	89.9	1–3	Sun and Gastinger, 1987 (Atlantic Richfield)
MeCl/BeO	430	1	ca. 0.6[a]	1-Butene	29.2	76.2	–	Sun, 1988 (Atlantic Richfield)
n-BuBr/MgO	430	1	ca.0.7[a]	1-Butene/2-Butenes=1/1	38	68.0	–	
6% WO_3/Al_2O_3	360	1	ca. 1.5[a]	1-Butene+ca. 0.025 atm. H_2O	42.6[b]	85.4[b]	1.25	Baker and Clark, 1987 (Flinders University)
9.3% SO_4^-, 31.1% ZrO_2/Al_2O_3	300	1	4.2[a]	1-Butene, C_4^-/N_2=1/5	–	–	1.5	Luy et al., 1988 (INCAPE)

TABLE 2 (Continued)

Catalyst type	Reaction temp. (°C)	Press. (atm)	Space velocity (g/g·h)	Feed and additives	Conversion (%)	i-$C_4^=$ (%) selectivity	Time-on stream (h)	Reference
Sn(HPO$_4$)$_2$·H$_2$O	430	–	0.4	1-Butene	25.1[b,c]	96.4[b,c]	1	La Ginestra, 1988 (Università 'La Sapienza,' and CNR, Rome)
20 ppm Pd, 3% SiO$_2$/Al$_2$O$_3$	500	1	ca. 1.1[a]	0.12% Propene, 16.24% n-Butane, 4.73% i-Butane, 10.14% 1-Butene, 67.67% 2-Butene, 1.10% i-Butene, H$_2$O/HC=1.33/1	33.5	94.1	–	Juguin and Martino, 1991 (IFP)
4.5% F/Al$_2$O$_3$	450	1	1.9	1-Butene, $C_4^=$/H$_2$O=1/0.23 0.121 N$_2$/min, $C_4^=$/N$_2$=1/9	49.3	66.9	5	Szabo et al., 1991 (Universities of Le Havre and Caen, and Total)
Theta-1	339	1	7.9	1-Butene, 1-$C_4^=$/N$_2$=1/8.3	86.6	35.6	71	Barri et al., 1987 (BP)
ZSM-22	550	1.6	21	1-Butene	39.8	94.5	–	Rahmin et al., 1992 (Mobil)
ZSM-23	500	1.2	160	1-Butene	38	90.6	–	Haag et al., 1992 (Mobil)
MgAPSO-31	550	1	93	1-Butene	44	77	–	Gaffney and Jones, 1992 (Arco)
SAPO-11	343	1	4.7	2-Butene	50.1	53.3	–	Gajda, 1992 (UOP)
Ferrierite	350	1.4	2	99.42% n-$C_4^=$, 0.44% i-$C_4^=$	50.9	80.9	336	Grandvallet, 1992 (Shell)

[a]Approximate value calculated from specified GHSV or LHSV, based on an assumed catalyst density of 1.0 g/ml.
[b]Calculated from given data.
[c]No indication given of amount of cracking or oligomerization products.

acidity and catalytic properties of fluorinated catalysts were summarized. Their review, however, did not cover the skeletal isomerization of linear alkenes. The kinetic modelling of the reaction has also been the subject of some previous reports [27,28].

This review of the literature on the catalytic skeletal isomerization reaction of the linear butenes is divided into three sections: the first and second sections dealing with halogenated and non-halogenated catalysts respectively covering the period up to 1991. The more recent work on zeolites and molecular sieves is covered in the third section. In Table 2, we have tabulated in chronological order the patents and papers, listing the catalyst type, the reaction conditions, the type of feed and additives, as well as selected catalytic results from each paper or patent. For the results in Table 2 and throughout this review, the following definitions hold:

% conversion $= \%\ i\text{-}C_4^= + \%$ non-$C_4^=$ in product stream

% selectivity $= [\%\ i\text{-}C_4^= / (\%\ i\text{-}C_4^= + \%$ non-$C_4^=)] \times 100$

% yield $= \%\ i\text{-}C_4^=$ in product stream $= (\%$ conv. $\times\ \%$ sel.$) / 100$

where $i\text{-}C_4^= =$ isobutene, and non-$C_4^= =$ products formed other than the butenes.

In our tabulation or discussion of the literature results and where only the percentage conversion and percentage selectivity are given, the percentage yield can be readily calculated from the equation given above.

2. HALOGENATED CATALYSTS

Most of the catalysts reviewed in this section were prepared by the addition of a halogen compound to alumina, except for those catalysts described in one of the patents, where the use of alkaline earth oxides is reported.

In a patent from IFP [29], the catalytic properties of fluorinated aluminas, for the skeletal isomerization reaction in the presence of water, were described. The catalysts were prepared by impregnating activated alumina with a solution of hydrofluoric acid. The solid was then dried at 100°C followed by calcination at 530°C. The olefin feed used was a C_4 cut whose composition is listed in Table 3.

The catalytic reactions were conducted at 450°C and a pressure of 1 atm using a catalyst with a fluorine content of 1% by mass. The influence of the water, which is co-fed with the hydrocarbon stream, was examined by varying the water/hydrocarbon (H_2O/HC) molar ratio (see Table 4). In the absence of water and at an LHSV $= 2$, high conversions of around 50% were obtained together with relatively low isobutene selectivities (50.3%) giving a 25.5% yield of isobutene. Under the above reaction conditions, rapid coking of the catalyst was also observed. With H_2O/HC $= 2.2$ and LHSV $= 1$, the conversion dropped to 40.9% but the selectivity increased to 89.4% (see Tables 3

TABLE 3

Composition of feed and product stream[a] obtained over fluorinated alumina [29]

Compound	Feed stream[a]	Product stream[b]
Methane	–	0.04
Ethane+ethylene	–	0.17
Propane	–	0.01
Propene	0.12	2.17
n-Butane	16.24	17.41
Isobutane	4.73	4.64
1-Butene	10.14	12.39
2-Butene	67.67	33.58
Isobutene	1.10	29.59
Polymers	–	–

[a]Obtained at 450°C, 1 atm, LHSV=1 and an $H_2O/HC=2.2$.
[b]Mass %.

TABLE 4

Effect of water and percentage F on catalytic properties of fluorinated alumina[a] [29]

F (%)	LHSV	H_2O/HC	Conversion (%)	Selectivity (%)	Yield (%)	Coke (%)
1	2	1.35	30.6	93.0	28.5	0.5
1	1	2.2	40.9	89.4[b]	36.6	0.2
1	2	–	50.7	50.3	25.5	28.3
1	2	11	13.2	95.6	12.6	0.01
0.05	2	1.35	4.5	95.7	4.3	0.01
10	2	1.35	43.6	71.2	31.0	0.6

[a] Obtained at 450°C and 1 atm.
[b] Detailed analysis is given in Table 3.

and 4). The yield of isobutene therefore increased from 25.5% to 36.6% (even at the lower LHSV) upon the addition of water to the feed stream (which also in effect reduces the partial pressure of the olefin to 0.3). At higher H_2O/HC levels, the conversion was found to decrease. Also in the presence of water, coking of the catalyst was minimal. It was further shown that decreasing the fluorine content to 0.05% resulted in a dramatic decrease in conversion whereas higher fluorine loadings gave lower selectivities. The usefulness of water in the feed stream and the levels of halogen required in fluorinated catalysts for the SI reaction of linear butenes was thus demonstrated. Similar results were obtained with this catalytic system in the skeletal isomerization of 1-pentene (35.2% conversion and a selectivity to isopentenes of 91.4%). However, since no information is given on the use of other additives or diluents, from the data given in this patent alone it is difficult to evaluate the

role of water, whether it is acting only as a diluent, resulting in lower partial pressures of the olefin, or actively influencing the catalytic sites.

This issue was addressed by Franz et al. [30] who examined in more detail the beneficial effect of added water on the activity, selectivity and life-time of fluorinated catalysts. Three separate experiments were conducted in which pure 1-butene was used, or was diluted with hydrogen or water. In the last two experiments the same level of dilution was used i.e. diluent/HC=0.4. The results obtained are shown in Fig. 4 and it can be observed that the addition of water (containing 40 ppm HF corresponding to the fluorine concentration in the aqueous phase downstream of the reactor) to the 1-butene feed resulted in a much slower deactivation of the catalyst while at the same time improv-
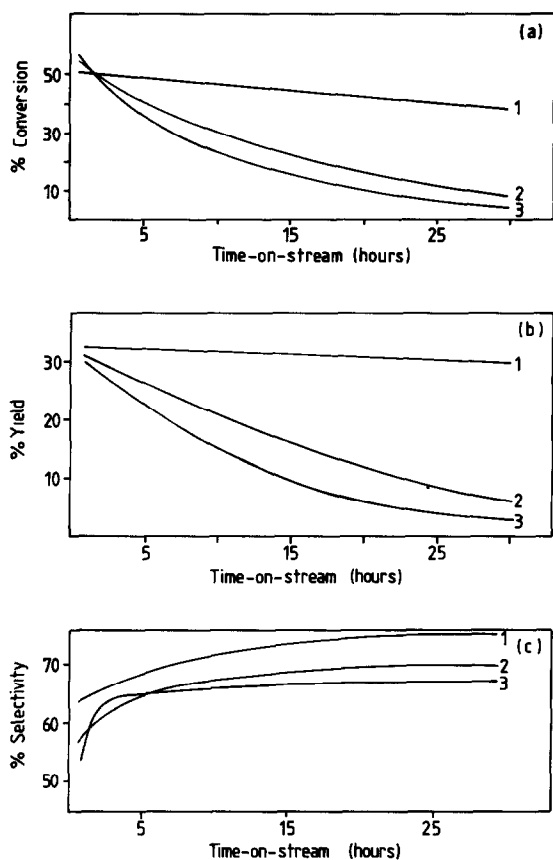

Fig. 4. Catalytic properties of fluorinated alumina. (a) Plot of percentage conversion versus time-on-stream; (1) with added water, (2) with hydrogen as diluent, and (3) with no added water or diluent. (b) Plot of percentage yield versus time-on-stream. (c) Plot of percentage selectivity versus time-on-stream; (1)–(3) as above [30].

ing the yield of isobutene, as compared with the runs where either no diluent or hydrogen was used. The use of water as additive therefore has a more pronounced effect than just that of an inert diluent such as hydrogen. The addition of water was not found to deactivate or damage the catalyst irreversibly. Fluorine is not immediately eluted from the catalyst and only a few ppm of fluorine are detected in the aqueous phase downstream of the reactor. The fluorine discharged from the catalyst is replenished by adding HF (or CF_4) to the fresh water stream. Regeneration of the catalyst by calcination at the reaction temperature was shown to be possible, provided that the fluorine is replenished, either continuously or discontinuously. Data on the activity and selectivity of the catalyst after twelve regenerations and 1000 hours of total operating time are reported [30]. Furthermore, the reaction was shown to proceed at 6 bar and with higher amounts of water (up to $H_2O/HC=4$ in the feed stream). Recycling of the water containing the fluorine effluent was found to be as effective as addition of the F-compounds to the feed water in maintaining catalyst activity. Replacement of the 1-butene feed with a C_4 cut, or an n-butene equilibrium mixture, or a cis/trans-2-butene mixture, or pure cis-2-butene, yielded similar results. In the experiment with the C_4 cut, the results show that the butanes behave as inerts. The isomerization of 1-pentene to isopentene was also carried out with results analogous to those obtained with the butenes.

Müller et al. [31] reported on the use of aluminas specially prepared from aluminium hydroxide and then impregnated with various halogen compounds such as BiOCl, BF_3, $ZrOCl_2$ or HCl. The catalytic reactions were carried out in the presence of hydrogen and were conducted in both fixed-bed and fluidized-bed reactors. With the latter, portions of the catalyst can be subjected to continuous or discontinuous removal to a regeneration unit and then fed back to the reactor after regeneration. Selected catalytic results from these systems are given in Table 2 where it can be observed that these catalysts produce yields of between 25-32% at MHSVs of about 3.8. The space-time yields of these catalysts are therefore higher than those of the catalytic systems surveyed previously. With only Al_2O_3 or with $ZrOCl_2$/commercial alumina as catalysts, both lower conversions and selectivities were obtained.

The effect of particle size and pore radii on the activity of alumina catalysts activated with methyl chloride (230-300 ppm in feed stream) was also examined [32]. It was shown that increasing the particle size from 0.7×10^{-3} to 317.5×10^{-3} cm and the percentage of pores having radii between 100 and 1000 Å from 13 to 32%, results in significantly lower yields of isobutene at MHSVs > 10. Some of the results have been tabulated in Table 5.

Eleazar and his co-workers [33], in their attempts to design a catalyst for the SI reaction that does not require frequent regeneration and high temperature, and to strike a balance between the production of isobutene on the one hand, and the production of alkanes on the other, investigated the use of a 1%

TABLE 5

Effect of particle size and pore size distribution on catalytic activity of alumina catalysts activated with methyl chloride [32]

Particle size (cm×10^{-3})	0.7	80	317.5
Surface area (m^2/g)	177	189	259
Pore volume (cc/g)	0.48	0.86	0.91
Pore size distribution:			
100 to 10 000 Å (%)	13	23	32.5
Less than 100 Å (%)	87	77	67.5
Reactor temperature (°C)	474–475	477–478	472–474
Inlet pressure (mmHg)	796	765–766	765
MHSV	10.3	15	15.6
Time-on-stream (h)	3.3	3.3	17.5
Conversion (%)	36.9	36.8	26.6
Selectivity (%)	95	93	91
Yield (%)	35	34	24

TABLE 6

Effect of n-butane (%) feed on activity and selectivity of halogenated 1% Pd/η-Al$_2$O$_3$ catalyst [33]

Hydrogen pressure (psia)	60	16
n-Butane in feed (%)	0.7	42.8
Total pressure (psig)	156	180
Conversion (%)	30.5	34.1
Selectivities (%)		
C$_{3+}$	1	1
n-Butane	16	4
Isobutane	2	2
Isobutene	78	85
Amylenes	1	2
C$_{6+}$	2	6
Yield (%)	24	29

Pd/η-Al$_2$O$_3$ catalyst pretreated with halogen compounds. This two-component catalyst, which is then treated with a third component (CCl$_4$), was used at 350°C and an MHSV = 0.5. The reactant also contained n-butane and hydrogen, the latter being used to suppress the formation of coke-forming hydrocarbons. The results obtained on increasing the amount of n-butane from 0.7 to 42.8%, i.e. to the dilution levels which will be encountered in industrial applications, are given in Table 6. The effect of pressure was also studied and it was observed that increasing the pressure from 13 to 26 atm increased the conversion from 34 to 51%, at the expense of lower selectivities. A catalyst cycle-time of 682 hours was indicated.

The preparation and use of brominated alumina catalysts have been described by Sun and Gastinger [34]. The bromine compounds employed for

the vapour-phase bromination of the aluminas included HBr, *n*-butyl bromide, methyl bromide and bromohydrin. The bromination of the oxides was carried out at 400°C and the catalytic evaluation at 425–450°C. From the latter it was observed that in terms of the activity and selectivity of these SI catalysts, the vapour-phase impregnation gave superior catalysts compared with the liquid-phase method, using, for example, an aqueous solution of NH₄Br (see Table 7). Other results showed that the addition of the halogen compounds can be carried out either in a continuous manner or in a pulse mode. It was also demonstrated that the activity of the catalyst can be maintained even by the recycling of the C_{5+} fraction which contains some of the eluted halogens. From their comparative studies with chlorinated and fluorinated catalysts, the authors concluded that the brominated aluminas were more active and selective for the SI reaction than either of the former two types of catalyst. A comparison of the data given in this patent with those obtained by Müller et al. and presented above, does not, however, show that brominated catalysts do indeed offer higher yields or higher space-time yields than, for example, chlorinated catalysts.

In another patent from the Atlantic Richfield Company [35], the use of halogenated alkaline earth oxides such as magnesium oxide, calcium oxide and beryllium oxide is reported. The skeletal isomerization catalysts were prepared by treatment of the above oxides with either bromine or chlorine compounds. The catalytic reactions were again conducted at temperatures around 430–450°C, but at much lower space velocities (GHSV = 270 h⁻¹) than those employed for the alumina catalysts (see Table 7). This could be an indication that halogenated alkaline earth oxides are of lower activity than the corresponding alumina catalysts. Further, a comparison of the results obtained with the three types of alkaline earth catalysts indicates that those of magnesium and beryllium (see Table 2) are more active than that of calcium.

Further information on the side-products arising from the parallel and consecutive reactions to the SI reaction, using a fluorinated alumina catalyst, was recently reported by Szabo et al. [15]. The reactions were studied as a func-

TABLE 7

Activities and selectivities obtained over brominated alumina catalysts [34]

Br source	HBr	NH₄Br (aq.)	*n*-BuBr	*n*-BuBr
Br quantity	50 ml	–	25 ml	210 ppm
Addition method	Pulse	Impregnation	Pulse	Continuous
Temperature (°C)	450	425	449	448
GHSV	1 250	1 200	1 050	1 035
Conversion (%)	29	<2	31.9	29.9
Selectivity (%)	91.4	–	88.0	89.9
Yield (%)	27	–	28.1	26.9

tion of temperature, 1-butene partial pressure, contact time and time-on-stream. The composition of the products formed over a range of temperatures is shown in Table 8. Formation of the dimer is favoured at low temperatures but decreases above 150°C and when the hydrocarbon pressure is reduced. It was also shown that the dimer formed is the source of the C_3 and C_5 species observed, that the by-products are important at all temperatures and that the yield of isobutene is highest (about 22%) between 400 and 450°C. At lower temperatures, the skeletal isomerization is too slow whereas at higher temperatures, the thermodynamics are unfavourable and side-products become too important even at moderate conversion levels. In this study, the effects of butene dilution, with nitrogen and water, were again examined (see Table 8). In agreement with the previous work described above, it was observed that the addition of water ($H_2O/HC=0.23$) to the feed markedly decreases the amount of by-products and enhances both the selectivity to isobutene (36% at the maximum) and the catalyst life-time. In terms of the dramatic influence of the water, the authors speculated that in the presence of water, the active sites are either blocked or converted into less active, but more selective, sites. Another conclusion reached is that as the activity drops with increasing time-on-stream, the rates of the secondary reactions decrease more markedly than that of the SI reaction, causing the concentration of isobutene to go through a maximum.

From the above survey of the publications on halogenated catalysts for the SI reaction, it can be concluded that this type of catalyst does exhibit sufficient activity and selectivity (at relatively high temperatures) for the skeletal isomerization reaction of both the linear butenes and pentenes. Further, the

TABLE 8

Conversion of 1-butene over fluorinated alumina: composition (wt.-%) of the products (space time $\tau=0.536$ h; catalyst age 5h) as a function of reaction temperature [15]

Temperature (°C)	300	450	450	450
N_2/C_4	2	2	9	9(+H_2O)
C_2	0.02	0.62	0.31	0.15
C_3	2.5	13.6	6.9	4.9
Isobutane +butane	2.9	9.8	1.9	0.7
1-Butene	12.2	5.7	11.7	13.7
Isobutene	10.5	13.2	24.0	33.0
trans-2-Butene	30.8	9.2	18.0	21.0
cis-2-Butene	20.8	9.6	13.8	15.9
Isopentane+pentane	0.15	0.85	1.3	0.24
Pentenes	8.9	22.0	12.1	8.1
C_6	5.3	8.9	9.9	1.9
C_7 +C_8	5.9	6.0	0.1	0.3
mol C_3/mol C_5	0.47	0.99	0.86	0.98
mol C_2/mol C_6	0.01	0.21	0.094	0.24

deactivation of the catalyst due to the elution of the halogens appears to have been minimized by either the continuous or intermittent addition of halogen to the feed. However, only in two reports is an indication given of the long-term stability of these catalysts. Also, the role of the halogens in corrosion promotion, especially that of fluorine, and the deleterious environmental effects of many halogenated organic compounds are well known. For these reasons, industrial processes which avoid the use of compounds of this type are likely to be more favourably received by industry and environmentalists alike. As a consequence, the following group of catalysts, described in Sections 3 and 4, represents a logical development away from the previous class, and it can be safely assumed that future catalytic research will concentrate more on non-halogenated catalysts.

3. NON-HALOGENATED CATALYSTS

As an alternative to, or an improvement on, the fluorinated alumina catalysts for the skeletal isomerization of *n*-butenes, Juguin and Miquel [36,37] described the preparation and use of a catalyst consisting of a γ-alumina of low alkali and alkaline-earth metals content, which had been impregnated with a solution containing ethyl silicate, aqueous palladium nitrate and ethanol. The preparation of these silicated aluminas was earlier described by the group at Snamprogetti [38]. After hydrolysis, drying and calcining, the final catalyst consisted of 3% silica, 20 ppm Pd and the balance alumina. The catalyst consisted therefore of alumina to which a specific amount of silica is added. The activity and selectivity of this silicated alumina catalyst were determined in both the presence and absence of water. As in the case of their previous work [29], the isomerization feed was a C_4 cut of the following composition: propene 0.1%, butanes 21.0%, isobutene 1.1% and linear butenes 77.8%. Operating temperature and pressure were 450 °C and 1 bar, respectively. The results (Table 9) show that a significant increase in isobutene yield is obtained (from 29.0 to 36.9%) for a simultaneous increase in water flow ($H_2O/$

TABLE 9

Influence of water and SiO_2 (%) on activity and selectivity of $Pd + SiO_2/Al_2O_3$ catalysts[a] [36,37]

Catalyst additives	LHSV	H_2O/HC	Coke (%) after 10 h operation	Conversion (%)	Selectivity (%)	Yield (%)
3% SiO_2 + 20 ppm Pd	2	1.35	0.4	31.5	91.9	29.0
3% SiO_2 + 20 ppm Pd	1	2.2	0.3	40.9	90.3	36.9
3% SiO_2 + 20 ppm Pd	2	–	25.5	51.7	46.7	24.1
11% SiO_2 + 20 ppm Pd	2	1.35	0.4	31.4	83.8	26.3

[a]At 450°C and 1 atm pressure.

HC = 2.2) and halving of the hydrocarbon flow. It can be noted that the yield of isobutene obtained here with the silicated aluminas is almost exactly equal to that obtained with the halogenated catalysts under the identical reaction conditions (Table 4). The results also show that a significant increase in coking is achieved when the water co-feed is omitted. However, a 10% decrease in isobutene yield is observed when the silica content is increased from 3% to 11%. The skeletal isomerization of 1-pentene was also examined over these catalysts. As indicated by Juguin and Miquel, the purpose of the palladium in the catalyst is to facilitate the regeneration of the catalyst, particularly for the combustion of high-molecular-weight products and coke which are deposited on the catalyst during the reaction. In the presence of palladium, lower regeneration temperatures are employed (starting temperatures of 200–250°C versus 325–375°C) and also lower oxygen concentrations, resulting in a lower combustion velocity.

Subsequently [39] it was shown that if the same type of catalyst (i.e. $Pd + SiO_2/Al_2O_3$) is prepared from spheres of alumina manufactured by coagulation in oil drops, rather than from cubic γ-alumina, then higher conversions and selectivities are obtained (Table 10). The experiments were again conducted in the presence of water ($H_2O/HC = 1.33$–1.35). In all of these studies on silicated aluminas [36,37,39], however, no indication is given of the catalyst cycle-times.

Silicated aluminas, prepared using different amounts of tetraethoxysilane, were also investigated by Nilsen et al. [40]. In this study, the catalytic experiments were conducted in the absence of water and the resultant selectivities were lower (Table 2) than those obtained by Juguin and his co-workers [36,37,39]. It was also observed by these workers that none of the silicated alumina catalysts showed higher selectivities than alumina itself. The catalysts with a low proportion of silicon gave much higher conversions and yields of isobutene than alumina. In the range of 0.75 to 6.1% SiO_2, the activity increased with surface silicon amount, but the selectivity to isobutene decreased. Further, the silication of alumina was found to improve the deactivation profile.

TABLE 10

Influence of type of alumina on activity and selectivity of $Pd + SiO_2/Al_2O_3$ type catalysts in the presence of water[a] [39]

Alumina type	Conversion (%)	Selectivity (%)	Yield (%)
Commercial cubic γ-Al_2O_3	31.5	91.9	29.0
Alumina prepared by coagulation in oil drops	33.5	94.1	31.5

[a] At 500°C, 1 atm, LHSV = 2, $H_2O/HC = 1.33$–1.35.

The effect of lanthanum addition to silicated aluminas, via impregnation with a lanthanum nitrate solution followed by calcination at 550°C, was studied by Stöcker et al. [41]. Once again it was shown that silicated alumina catalysts gave high yields of isobutene, but the activity of the catalysts decreased with increasing La content (Table 11). Using unmodified alumina as catalyst, the yield of isobutene was approximately 1/10 of that of the silicated material.

Another evaluation of silicated aluminas, which included characterization by elemental analysis, X-ray photoelectron spectroscopy, infrared spectroscopy and reaction kinetics using the SI reaction of 1-butene as the catalytic test reaction, has been reported by Nilsen et al. [42]. The catalysts were prepared by the condensation reaction of tetraethoxysilane with the surface of the alumina. The silicon-containing groups that formed on the alumina surface, at less than monolayer coverage, induced strong acidity. The presence of both Brønsted and Lewis acid sites was detected by infrared spectroscopy. The catalytic reaction was carried out in a flow reactor at atmospheric pressure and at 450–525°C. The reaction was found to be first order in the reactant, and the activity increased with increasing surface acidity, i.e. with increasing Si content of the surface and apparently with increasing Brønsted acidity. A comparison of the activities of the commercial silica–alumina and silicated–alumina (6 wt.-% SiO_2) catalysts prepared by the reaction of $Si(OC_2H_5)_4$ with the Al_2O_3 surface indicates that activity exceeding that of silica–alumina can be achieved when Si is restricted to a monolayer (see Fig. 5). It was inferred, on the basis of the similarities in catalytic activity and infrared spectra, that the catalytic sites are nearly the same in the two classes of materials.

TABLE 11

Skeletal isomerization of 1-butene over La-modified silicated alumina at 475°C[a] [41]

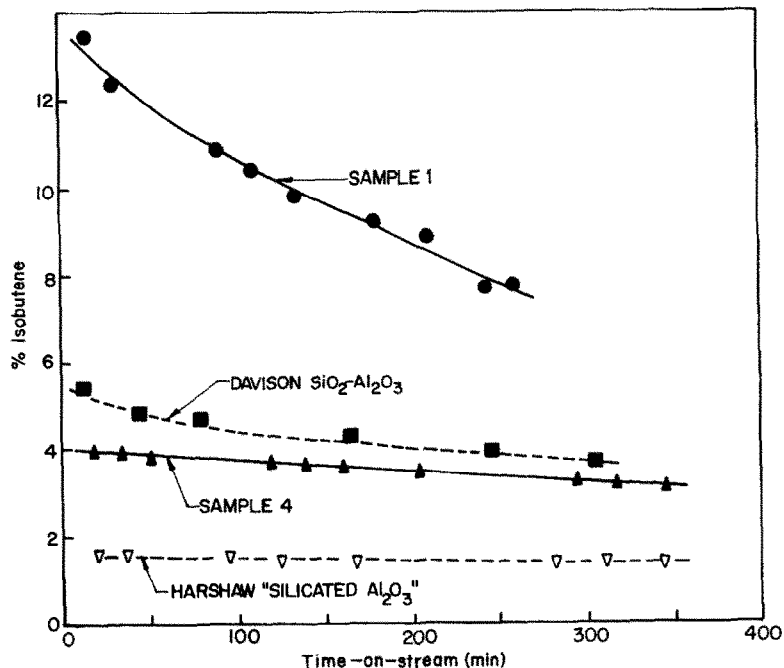| Amount of		Yield of isobutene (%)	Selectivity to isobutene (%)
Si (%)	La (%)		
0	0	2.5	55
0	3.1	0.5	70
0	4.5	0.3	55
1.1	0	20	77
1.1	2.5	1.5	85
1.1	4.9	0.5	70
2.4	0	19	75
2.4	2.5	5.5	65
2.4	5.2	2.0	70

[a]Measured at 6 h on-stream, WHSV = 2.

Fig. 5. Activities and stabilities of commercial silica–alumina catalysts compared with those prepared from [Si(OC$_2$H$_5$)$_4$] and Al$_2$O$_3$ (samples 1 and 4; 2.9 and 0.96 Si groups per nm respectively). Conversion determined at 500°C, 1 atm, 1-butene partial pressure of 0.57 atm and space velocity of 2.2×10^{-5} mol/(g of cat·s) [42].

Recently, Basini et al. [43] studied the gas-solid interaction phenomena occurring during the catalytic reaction over silicated alumina by vibrational spectroscopic experiments. This was done both with transmittance experiments on self-supported wafers of solid samples and with diffuse reflectance investigations inside the catalytic reaction environment in a plug-flow microreactor. The spectra recorded during the interactions led the authors to propose that the catalytic isomerization occurs through a temperature-dependent proton transfer equilibrium between an OH surface group and an H-bonded internal olefin.

In a patent by Myers and Strope [44], it was demonstrated that even pure alumina, without any other catalyst additive, was also an active and selective catalyst for the SI reaction at 480°C, provided water is added to the olefin feed (at 3.34 mol-%) or to the regeneration gas (N$_2$/air=10/1). The data (Table 12) show that the presence of water in the n-butene feed results in an increase in both the conversion and selectivity and that the presence of water in the butene feed is more effective than the presence of water in the regeneration gas. In other experiments it was observed that water in the feed causes a greater retention of catalyst activity than the presence of water only in the

TABLE 12

Influence of water on catalytic activity and selectivity of alumina[a] for the I reaction[b] [44]

H$_2$O content (mol-%)	0	3.34	3.34	0
Regeneration gas	dry	dry	wet	wet
Time-on-stream (h)	1	1	1	0.5
Conversion (%)	14.0	35.5	40.3	25.9
Selectivity (%)	53.7	68.8	65.3	81.5
Yield (%)	7.5	24.4	26.3	21.1

[a]Catapal alumina, surface area 219 m^2/g, sodium content 0.003 mass%, pellets 1/16 in.
[b]At ca. 480°C, 1 atm and LHSV = 2.0

regeneration gas. The only pretreatment carried out on the alumina was drying at 350°C for four hours under nitrogen. This beneficial effect of the small amounts of added water on the skeletal isomerization activity of alumina was also presented in an earlier paper [45]. It can thus be concluded that the improvement in activity and selectivity for the SI reaction, upon addition of water to the feed streams, applies to the cases of both halogenated and non-halogenated catalysts and even to alumina itself. Further understanding of this beneficial effect of the water could help in the designing of better catalysts for this reaction.

Since the addition of SO$_4^{2-}$ to supports such as ZrO$_2$, TiO$_2$, Fe$_2$O$_3$ and HfO$_2$ produces an enhancement in their catalytic activities for acid-catalyzed reactions, Luy et al. [46] studied the activity of a series of sulphated ZrO$_2$/Al$_2$O$_3$ samples. The catalysts were prepared by impregnating γ-Al$_2$O$_3$ with repeated applications of an aqueous solution of zirconyl chloride at room temperature, followed by washing with NH$_4$OH solution and impregnation with a dilute solution of H$_2$SO$_4$. The materials were then dried, calcined and kept under helium until used. These catalysts, together with a sulphated alumina, a pure alumina and a pure silica–alumina were tested in an isothermal plug-flow reactor at the relatively low temperature of 300°C and at 1 atm, where the mass of each catalyst was adjusted so as to obtain the same catalyst surface area in the reactor (75 m^2). The catalysts were activated at 500°C for two hours in air flow. Table 13 lists the initial conversions extrapolated to zero time and, in parentheses, the conversion obtained at 90 minutes on-stream. Pure Al$_2$O$_3$ yielded equilibrium values for the three linear butene isomers, with no skeletal isomerization evident. With SiO$_2$–Al$_2$O$_3$, only traces of isobutene were detected. The addition of ZrO$_2$ to Al$_2$O$_3$ produced a very sharp decrease in the conversion to the cis/ trans-2-butene. However, when the sulphate was added to ZrO$_2$/Al$_2$O$_3$, not only was the n-butenes equilibrium distribution observed, but significant amounts of the skeletal isomer were also formed. Conversion to isobutene showed an increase with increasing ZrO$_2$ content. Further, sulphate ion addition to pure Al$_2$O$_3$ also yields isobutene, although

TABLE 13

Specific surface areas of, and conversions[a] obtained over, sulphated ZrO_2/Al_2O_3 and other catalysts at 300 °C [46]

Catalyst	S_g (BET) (m^2g^{-1})	Conversion (%)		
		cis-2-$C_4^=$	trans-2-$C_4^=$	i-$C_4^=$
Al_2O_3	200	31.9 (31.9)	49.6 (49.6)	0 (0)
SiO_2–Al_2O_3	559	31.4 (31.4)	49.2 (49.2)	Traces (tr)
1.6% ZrO_2/Al_2O_3	190	12.4 (12.5)	6.3 (6.3)	0 (0)
6.5% ZrO_2/Al_2O_3	177	0.8 (0.8)	1.1 (1.1)	0 (0)
15.4% ZrO_2/Al_2O_3	156	1.9 (1.9)	1.3 (1.3)	0 (0)
1.6% ZrO_2/Al_2O_3 +7.1% SO_4^{2-}	193	28.5 (30.4)	46.5 (48.1)	8.8 (4.3)
6.5% ZrO_2/Al_2O_3 +6.6% SO_4^{2-}	184	30.3 (30.7)	47.8 (48.4)	9.0 (3.3)
14.3% ZrO_2/Al_2O_3 +9.1% SO_4^{2-}	172	22.6 (30.8)	48.9 (48.0)	10.0 (4.0)
31.1% ZrO_2/Al_2O_3 +9.3% SO_4^{2-}	174	28.9 (31.1)	44.8 (46.1)	13.5 (5.8)
Al_2O_3 +8.0% SO_4^{2-}	184	30.2 (31.1)	46.6 (48.2)	7.8 (3.2)

[a]Initial conversion extrapolated to zero time and, in brackets, values obtained at 90 min on-stream.

the effect is not as significant as in the case of ZrO_2/Al_2O_3. For all these systems, however, the yield of isobutene obtained was far below the equilibrium value.

The improvement of the selectivity of SI catalysts via the neutralization of some of the acid sites has also received attention [47]. The approach used involves the exchange with alkali metal cations of the acid sites on the surface of the support or binder, whereas the acid sites of the zeolite or molecular sieve catalyst are not exchanged to a high degree. This selective exchange is achieved through the employment of organic ligands which can complex the metal cations but are too large to enter the pores of the molecular sieve. The organic ligands, dissolved in toluene, can thus transport the complexed cation to the unhindered support acid site, but because of their size, cannot transport the cation to the acid sites situated in the pores of the sieve. As a consequence, the latter type of acid sites are not neutralized to a large extent. For the catalyst under investigation (20% borosilicate in alumina), it was shown that the partially neutralized system exhibited a considerable increase in selectivity (from 36.6 to 66.3%) with a concomitant decrease in activity (from 64.5 to 36.5% conversion) which gave, however, the same percentage yield of isobutene. The data, therefore, did not demonstrate the beneficial effect of the neutralization process other than to maintain the inverse relationship between conversion and selectivity.

In another report [48] the use of a "silicalite type" catalyst for the skeletal isomerization of n-butenes was described. It was shown that with this type of catalyst, and under the reaction conditions employed (see Table 2), high con-

version together with extremely low selectivities to isobutene (< 16%) were obtained, even in the presence of steam.

Another group of compounds that has been investigated as catalysts for the SI reaction are the phosphates. In the paper by Nilsen et al. [40], results are presented on the maximization of both the surface areas and catalytic activities of various boron phosphate preparations, silicated boron phosphate and boron phosphate supported on both alumina and silicated alumina. The catalytic evaluations were carried out at 475°C and with an MHSV = 2. The results indicated that the silication of the boron phosphate appears to stabilize the surface area and substantially improve the catalytic activity of the systems (yield of isobutene increased from 24 to 36%). In contrast to the non-silicated catalyst, the silicated equivalents maintained their high selectivities throughout the run (up to 6.5 hours on-stream). The effects of the calcination and silication temperatures, the type of silicating agent, steaming and the P/B ratio were found to be small, as long as the silicon content was in the range of 8–15%. The boron phosphate/alumina catalysts exhibited similar activities to, but better selectivities than, the silicated alumina catalysts. A significant difference between these last two types of catalysts was in the type of byproducts produced. The silicated boron phosphate produced mainly C_8, whereas the silicated alumina produced C_{5+}, indicating a higher cracking activity for the latter catalyst which in turn shows that the silicated aluminas have sites of stronger acidity.

La Ginestra et al. [49] reported on their investigation into the catalytic activity of several crystalline tin phosphates, prepared by different methods such as refluxing or hydrothermal treatment. The results showed that the acidic properties of these materials strongly depend on the values of the different physical and chemical parameters characterizing their preparation or the thermal pretreatment of the catalysts. Despite the similarity of the X-ray powder patterns of the various tin phosphates, the chemical, thermoanalytical and catalytic data were different. The latter were obtained from the SI reaction of 1-butene at 430°C (after pretreatment in air at 450°C). The results showed that the most active materials for the skeletal isomerization reaction were the less crystalline materials. Their activity increased with increasing P/Sn ratio above the stoichiometric P/Sn = 2. A typical result is given in Table 2. No indication, however, is given of any side-products. The strong acid sites of the tin phosphates, presumably responsible for the SI reaction, were attributed to an excess of adsorbed phosphoric acid.

A study on the preparation, conditioning and use of a catalyst consisting of tungsten oxide/alumina has also appeared [50]. The catalyst was prepared by impregnating an alumina sample with sodium tungstate, followed by drying, washing with acid and drying at 160°C. Catalytic activity was only achieved after a partial reduction of the yellow WO_3 component of the catalyst to a dark blue oxide. The catalytic isomerizations of 1-butene, 1-pentene and 1-

hexene were carried out as a function of preconditioning treatment and type of carrier gas. For 1-butene, the use of H_2/H_2O for preconditioning at 380°C and as carrier gas promoted the longest catalyst life-time. It appears that the feed stream should contain some hydrogen, since running in argon resulted in rapid catalyst deactivation. Pretreatment in hydrogen only did not produce any significant differences in the case of 1-butene. It did, however, make a difference in the reaction of 1-pentene. The different preconditioning and regeneration procedures and carrier gas requirements for each of the two alkenes are discussed in detail by the authors. It was also noted that the reaction conditions employed did not favour the metathesis reaction. The skeletal isomerization reaction of higher alkenes such as 1-octene and 1-dodecene and a Fischer–Tropsch product was also examined.

4. ZEOLITES AND MOLECULAR SIEVES

Barri et al. [51] reported on the suitability of ZSM-5, ZSM-23 and Theta-1 zeolites as catalysts for the SI reaction. Using a diluted stream (N_2/HC = 8.3) it was found that Theta-1 is more than three times more selective for isobutene formation than ZSM-5 (at 377–379°C, MHSV = 7 and 1 atm, see Table 14). The Theta-1 zeolite produced considerably less of the undesirable lower and higher than C_4 hydrocarbons. It was also determined that the C_{5+} produced over Theta-1 was mainly alkenes whereas that obtained over ZSM-5 contained significant amounts of alkanes. The high yields of isobutene observed with the Theta-1 zeolite, relative to ZSM-5, can be ascribed to the smaller channel diameters of the former (i.e. 5.5×4.4 Å for Theta-1 and 5.6×5.3 and 5.5×5.1 Å for ZSM-5). The narrower channels therefore appear to be preventing the dimerization of the feed or of the product isobutene due to steric constraints.

In the case of the undiluted feed, all these catalysts (ZSM-5, ZSM-23 and Theta-1) gave low selectivities to isobutene (< 10 mol-%). Again using the diluted feed, the effect of reaction temperature was studied as well as the regeneration of the catalyst. The results showed (Table 15) that increasing yields

TABLE 14

Conversions and selectivities[a] obtained over ZSM-5 and Theta-1 zeolites [51]

Catalyst	Temperature (°C)	Conversion (%)	Selectivities (%)						
			C_{1-3}	$C_2^=$	$C_3^=$	C_4	$2C_4^=$	i-$C_4^=$	C_{5+}
ZSM-5	377	96.6	6.2	4.8	20.9	14.5	10.9	11.2	31.5
Theta-1	379	90.0	0.9	0.8	10.6	3.8	33.7	35.0	15.2

[a]In mol-%, at 1 atm, MHSV = 7.2 and $N_2/C_4^= = 8.3$.

TABLE 15

Conversions and selectivities[a] obtained over Theta-1 as a function of reaction temperature and regeneration [51]

Temperature (°C)	Conversion (%)	Selectivity (%)			
		C_{1-4}	$2\text{-}C_4^=$	$i\text{-}C_4^=$	C_{5+}
234	85.1	0	92.1	7.1	0.8
276	84.5	0.8	83.6	13.9	1.7
326	87.9	3.8	54.3	36.0	5.9
376	89.2	6.6	41.8	43.7	7.9
Zeolite regenerated in air at 550°C for 16 h					
376	87.5	5.3	41.9	40.6	12.2
426	87.7	7.9	41.7	42.1	8.3
475	86.1	8.6	42.8	42.0	6.6

[a]In mol-%, at 1 atm, MHSV = 7.6–9.0 and $N_2/C_4^= = 7.7$.

of isobutene are obtained as the temperature is increased from 234 to 376°C and that regeneration of the zeolite, in air, does not have any deleterious effect on the activity of the catalyst. Other results given in the patent show that the % of C_{5+} can be decreased by using higher space velocities (2 to 26 h^{-1}) which at the same time increase the % of isobutene. The performance of the catalyst with time-on-stream, again using the diluted stream, was also evaluated and it was shown that after 71 hours on-stream the % conversion decreased only slightly, from 89.5 to 86.6%, whereas the selectivity to isobutene increased from 29.0 to 35.6%. In other experiments it was observed that lower calcination temperatures (e.g. 325 versus 500°C) result in higher yields of isobutene (25.5 versus 4.6 mol-%) when using a pure 1-butene feed. The use of the lower calcination temperatures (which presumably give only partial removal of the template) and lower olefin partial pressures also resulted in higher selectivities to isobutene. From the results detailed in this study, it can be concluded that at relatively low reaction temperatures (below 400°C) and with diluted feed streams, zeolites such as Theta-1 can produce high yields of isobutene with fairly good stabilities with time-on-stream.

A substantial advantage arising from the use of zeolitic catalysts is that they allow the reaction to proceed at lower reaction temperatures (probably due to their stronger acidity relative to that of the halogenated and other amorphous catalysts described in the last two sections), thus affording *higher* equilibrium concentrations of the branched isomer.

The catalytic properties of Theta-1 were compared by Rahmin et al. [52] to those of its isotype ZSM-22 [53] at higher temperatures (400–550°C) and at considerably higher MHSVs (21 and 75 h^{-1}) and where the crystallite size of the ZSM-22 used was below 0.5 microns and that of Theta-1 was up to 2

microns. From the results shown in Table 16 we can observe that the micro-crystalline ZSM-22 catalyst has significantly higher activity than the large crystal Theta-1 at 400°C and MHSV = 75. Increasing the temperature to 550 °C, however, results in approximately the same percentage yield of isobutene by both catalysts.

The use of the narrower-pore zeolite ZSM-23 (4.5 × 5.6 Å) was also examined [54] at high temperatures (500°C) and at even higher space velocities (160 h^{-1}). The yields of isobutene obtained ranged between 27% and 35% (see Table 2).

The application of molecular sieves as catalysts has also been the subject of recent investigations. Gaffney and Jones [55] examined the catalytic properties of the sieve MgAPSO-31 at high temperatures and high space velocities. Highest yield of isobutene (33.9%) was achieved at 550°C, 1 atm and MHSV = 93. In contrast, the study on SAPO-11, with pore diameters of 6.3 × 3.9 Å, was carried out at low temperatures and low MHSVs [56]. At 343°C and an MHSV = 4.7, the yield of isobutene was 26.7% (Table 2).

The last catalytic system to be reviewed is that described in a recent Shell patent [57] which is based on the zeolite ferrierite. It was found that with this narrow pore zeolite (4.2 × 5.4 and 3.5 × 4.8 Å) the conversion of the linear butenes can be carried out at low temperatures (350°C), a total olefin pressure of 1.4 bar, MHSV = 2 and in the absence of any diluent, with high activity and selectivity and with excellent stability with time-on-stream. The results obtained show (Table 17) high yields of the branched alkene which actually increase with time-on-stream.

As in the case of the Theta-1 work, low temperatures were again employed with ferrierite thus giving the higher equilibrium yields. The main difference

TABLE 16

Comparison of ZSM-22 and Theta-1[a] [52]

WHSV	Temp. (°C)	N$_2$/HC	Conv. (%)	Sel. (%)	Yield (%)
Microcrystalline ZSM-22					
75	400	3	44.3	61.1	27.1
75	550	3	40.6	88.1	35.8
21	400	10	40.4	83.3	33.6
21	550	10	39.8	94.5	37.6
Theta-1					
75	400	3	3.6	87.7	3.2
75	550	3	34.9	94.5	33.0
21	400	10	26.6	90.5	24.1
21	550	10	35.2	94.5	33.3

[a]At 1.6 atm.

TABLE 17

Conversion of n-butenes over ferrierite as a function of time-on-stream[a] [57]

Product	Mass %	
	48 h	336 h
C_1–C_2 paraffins	0	0
Ethene	0.04	0.01
Propane	0.07	0.02
Propene	1.7	0.8
Butane	1.3	0.8
n-Butene	40.1	49.1
Isobutene	37.0	41.2
C_{5+}	19.9	8.0

[a]At 350°C, 1.4 atm and MHSV = 2.

between the two zeolites is, however, that the ferrierite zeolite is able to produce the high yields of isobutene without any feed dilution. Another dissimilarity between the two zeolites is that whereas the calcination of Theta-1 at 500°C, in order to remove the template, results in low yields of isobutene when a pure butene feed is used due to extensive C_{5+} formation, in the case of ferrierite the same calcination temperature results in a zeolitic catalyst with good SI properties. It can thus be concluded, from the studies by Barri [51] and Grandvallet et al. [57], that the narrower-pore zeolites are the most promising catalysts for industrial application. Further work is, however, needed to ascertain whether the channel dimensions such as those found in ferrierite are indeed the ideal ones for the skeletal isomerization of 1-butene, or whether even narrower pore zeolites can offer higher yields of the branched isomer.

5. CONCLUSIONS

Since the late 1970s tremendous progress has been achieved in the catalytic conversion of linear butenes to isobutene. In Section 2 we surveyed the catalytic properties of halogenated catalysts. Even though this type of catalyst, e.g. halogenated alumina, has been shown to exhibit sufficient activity and selectivity, the corrosion and environmental problems associated with these materials are most likely to prevent their industrial application. From the survey on the non-halogenated catalysts and zeolites, presented in Sections 3 and 4, it appears that the narrow-pore zeolites, e.g. ferrierite, is the group of catalysts that are suitably active, selective and stable with time-on-stream in terms of the SI reaction. Their catalytic properties can be ascribed to (i) the high acid strength of the zeolitic active sites which allows the reaction to proceed at the

relatively lower reaction temperatures thus affording the higher equilibrium concentrations of the branched isomer, and (ii) the narrower channels which appear to prevent the subsequent dimerization, etc of the feed or of the product isobutene, due to steric constraints. As a consequence, these zeolitic catalysts could therefore be the choice of type of catalyst for future industrial implementation of the skeletal isomerization reaction. Indeed, ferrierite is the type of catalyst used in Lyondell Petrochemical Company's single-step catalytic process for the conversion of linear butenes to isobutenes [58] which was announced early in 1992 [59]. Lyondell disclosed that a large-scale demonstration plant for the process is planned for this year with the possible building of a commercial unit at its Channelview location after two years.

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