

Conversion of Butane to Isobutane in the Presence of Solid Super Acid and Friedel-Crafts Catalysts

MICHAEL STÖCKER* and BJØRN PETTER NILSEN**

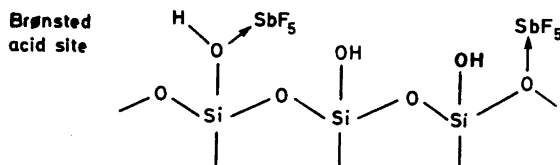
Department of Petrochemistry, Central Institute for Industrial Research,
P.O.Box 350 Blindern, N-0314 Oslo 3, Norway

Among the acid catalyzed isomerization of alkanes, the conversion of butane to isobutane is the slowest. It is known that isobutane is formed via a primary carbonium ion, and the low stability of this ion is responsible for the slow butane isomerization.¹ In order to get a useful yield of isobutane the reaction should be carried out with effective catalysts and at higher temperatures. On the other hand, temperature also plays a vital role in control of product distribution since the formation of isobutane is thermodynamically favored at low temperature. Several attempts have been made to study the conversion of butane and to find a compromise concerning the reaction temperature. Hattori *et al.* succeeded in synthesizing solid super acids, such as SbF_5 , supported on different metal oxides, which are catalytically active for the reaction of butane at room temperature.^{2,3} Sulfate-treated zirconia and titania were used by Arata *et al.* for the isomerization of butane at 50 °C (for TiO_2) and 25 °C (for ZrO_2).⁴⁻⁶ Conversions of butane at different temperatures in the presence of solid catalysts prepared by the reaction of AlCl_3 with each of the following supports, silica, sulfated silica, sulfonated silica and sulfonated macroporous poly-styrene-divinyl-benzene (Amberlyst 15) have been reported by Gates *et al.*^{7,8} Crathorne *et al.* presented SbF_5 supported on SO_2 -treated alumina as an active catalyst at 65 °C.⁹

Recently, the isomerization of hexane catalyzed by Friedel-Crafts and solid super acid catalysts were studied by our group.¹⁰ The carriers treated with SbF_5 were the most active catalysts when the reaction was carried out at low temperature. Our intention was, therefore, to study the catalytic behaviour of these systems in reactions of butane. Furthermore, isobutane is known as an important feedstock since this compound is used in several technical processes, *e.g.*, alkylation of isobutane with light olefins. This work deals with the isomerization of butane catalyzed by SbF_5 - SiO_2 , SbF_5 - SiO_2 - TiO_2 , SbF_5 -Amberlyst 15, AlEtCl_2 - SiO_2 , AlEtCl_2 - SiO_2 - TiO_2 and BF_3 - SiO_2 .

Results and discussion. The results on isomerization of butane are collected in Table 1. Small amounts of pentanes were formed in addition to isobutane. The product distributions were found to be constant after the time mentioned in the table. Since the product distributions were observed to be far from the equilibrium concentration, we presume that the catalysts were deactivated after this time.

As shown in Table 1, the SbF_5 -treated catalysts were active for the skeletal isomerization of butane at 30 °C. Isobutane was produced in 5–7.5 % yield, except in the case of SbF_5 -Amberlyst 15. This is in line with the findings reported by Hattori *et al.*³, who found the SbF_5 -based catalysts to be the most effective systems for the isomerization of butane. In the catalyst, SbF_5 probably interacts with the surface hydroxyl groups. The structure of the acidic sites on SbF_5 - SiO_2 may be drawn as follows (Scheme 1):



Scheme 1.

* Author to whom correspondence should be addressed.

** Present address: Statoil, P.O.Box 300 Forus, N-4001 Stavanger, Norway.

Table 1. Reaction of butane over acid catalysts at 30 °C.

Catalyst	Calcination temp./°C	Time/h	Distribution of products/% ^a				Conversion/%
			I-C4	N-C4	I-C5	N-C5	
SbF ₅ -SiO ₂	200	44	6.1	93.6	0.2	T ^b	6.3
		670	7.6	92.0	0.3	T	7.9
SbF ₅ -SiO ₂	400	50	5.7	93.8	0.4	0.1	6.1
		168	7.1	92.2	0.5	0.1	7.7
SbF ₅ -SiO ₂	600	481	5.2	94.5	0.2	T	5.4
SbF ₅ -SiO ₂ -TiO ₂	200	213	7.5	92.1	0.4	T	7.8
SbF ₅ -SiO ₂ -TiO ₂	600	214	7.5	91.9	0.4	0.1	8.0
SbF ₅ -Amberlyst 15		213	1.7	98.1	0.1	T	1.8
AlEtCl ₂ -SiO ₂	200	355	0.6	99.4	0	0	0.5
AlEtCl ₂ -SiO ₂	600	339	0.1	99.8	T	0	0.1
AlEtCl ₂ -SiO ₂ -TiO ₂	200	643	2.3	97.7	T	T	2.3
AlEtCl ₂ -SiO ₂ -TiO ₂	600	332	0.6	99.4	T	0	0.5
BF ₃ -SiO ₂	200	310	0.1	99.9	T	0	0

^a I-C4: isobutane; N-C4: n-butane; I-C5: isopentane; N-C5: n-pentane; traces of propane were observed. ^b T=trace.

The coordination of SbF₅ to the hydroxyl groups will increase the acid strength of the OH groups (Brønsted acid sites) and, therefore, the catalyst becomes more active. Furthermore, Hattori *et al.*³ reported that the metal halide reacted with the surface hydroxyl groups at higher temperature to give -OSbF₄ and HF. Since the formation of HF molecules could not be detected, he supposed that the HF produced may react with another hydroxyl group to form H₂O and the fluorine bound to Si. These findings are in agreement with corresponding investigations made by our group concerning the anchoring of TiCl₄ on silica.¹¹ Also the reported Hammett H_0 -values for the SbF₅-SiO₂ and SbF₅-SiO₂-TiO₂ catalysts of about $-13.16 \geq H_0 > -13.75$ ³ were in line with our measurements,¹² indicating a strong acid strength for the SbF₅-containing catalysts. The AlEtCl₂- and BF₃-based catalysts were completely or almost inactive. This might be due to extreme long induction periods for these catalysts. A shortening of the induction period may be obtained by the use of a promotor, such as organic halids or HCl in the feed. Gates *et al.*⁸ succeeded in the synthesis of supported AlCl₃ catalysts, which increased the rate of the butane isomerization by using HCl in the feed to a flow reactor. The selectivities of the catalysts for the skeletal isomerization were in the range of 83–94 %. Only small variations in conversions were observed for the reaction of butane over SbF₅-treated metal oxides. The activity did not depend upon the kind of metal oxide (single or binary component system) and not upon the preparation conditions, *i.e.*, calcination temperature.

From the examination of our results it was concluded that the use of the SbF₅-based solid super acids provided conversions at room temperature. The deactivation properties of the SbF₅-containing catalysts should be improved and the use of promotors for the AlEtCl₂-based system is recommended.

Experimental. The syntheses of the catalysts have been published in a previous paper by our group.¹⁰

The reactions were carried out in 3 ml glass micro reaction vessels (Supelco, Inc.), equipped with teflon constructed Mininert valves. 2 ml butane (liquid phase, J.T. Baker Chem. B.V., 99.9 % purity) were allowed to react over 100 mg of the catalyst at 30 °C. The reaction products were periodically withdrawn from the reaction system and analyzed by gas chromatography (Hewlett Packard 5880). A 60 m glass capillary column with methyl silicone (SP 2100) was employed operating at the following temperature profile. Initial value: 5 °C for 5 min; program rate: 2 °C/min for 10 min. The percentage conversions were obtained by measuring peak areas.

Acknowledgements. The authors are indebted to Aud Spjelkavik and Arild Andersen for their technical assistance. Our thanks are due to the Royal Norwegian Council for Scientific and Industrial Research for financial support.

1. Gates, B.C., Katzer, J.R. and Schuit, G.C.A. *Chemistry of Catalytic Processes*, McGraw-Hill, New York 1979, p. 23.
2. Tanabe, K. and Hattori, H. *Chem. Lett.* (1976) 625.
3. Hattori, H., Takahashi, O., Takagi, M. and Tanabe, K. *J. Catal.* 68 (1981) 132.
4. Hino, M. and Arata, K. *Chem. Commun.* (1979) 1148.
5. Hino, M. and Arata, K. *Chem. Commun.* (1980) 851.
6. Hino, M., Kobayashi, S. and Arata, K. *J. Am. Chem. Soc.* 101 (1979) 6439.
7. Magnotta, V.L. and Gates, B.C. *J. Catal.* 46 (1977) 266.
8. Fuentes, G.A., Boegel, J.V. and Gates, B.C. *J. Catal.* 78 (1982) 436.
9. Crathorne, E.A., Howell, I.V. and Pitkethly, R.C. *U.S. Pat.* 3 975 299 (1976).
10. Stöcker, M. and Nilsen, B.P. *Acta Chem. Scand. B* 38 (1984) 55.
11. Riis, T., Dahl, I.M. and Ellestad, O.H. *J. Mol. Catal.* 18 (1983) 203.
12. Riis, T. *Royal Norwegian Council for Scientific and Industrial Research, Report No.* 74 01 03-9, Central Institute for Industrial Research, Oslo 1980, p. 19.

Received August 3, 1984.