# Isomerization of Hexane Catalyzed by Friedel-Crafts and Solid Super Acid Catalysts

MICHAEL STÖCKER* and BJØRN PETTER NILSEN**

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

The isomerization of hexane was carried out at 30 and 100 °C, over solid acid catalysts which were prepared by treatment of silica, silica-titania and Amberlyst 15 with $AlEtCl_2$, $SbF_5$ and $BF_3$ under different conditions. The preparation conditions which affected the catalytic behavior of the catalyst were studied. The $SiO_2-TiO_2$ system became the most active catalyst when treated with $SbF_5$. The maximum conversions were obtained after different reaction times depending on the deactivation of the catalysts. The maximum conversion was high when the metal oxide was calcined at a low temperature and also when the reaction was carried out at low temperature.

Considerable effort has been devoted to the study of the isomerization of hydrocarbons such as pentanes and hexanes.[1-7] The increasing demand for low-lead and non-leaded gasolines has increased the importance of industrial processes by which low-octane, straight-chain alkanes are isomerized to high-octane isoalkanes.[8]

The mechanism for the skeletal isomerization of alkanes is well known, both for the reactions catalyzed by homogeneous systems[1-5] and the processes carried out by heterogeneous catalysts such as solid super acids.[6,7]

From a thermodynamic point of view the isomerization of hexane should operate at a low temperature level as this favours a high equilibrium concentration of iso-derivatives.

A variety of catalysts which are active for the isomerization of hexane at low temperature has been studied. The $AlCl_3-Al_2O_3$ system of Krzywicki et al. operates at 100 °C.[9] Olah succeeded in the synthesis of solid catalysts based on fluorinated graphite such as $SbF_5-HSO_3F-$ graphite, which are catalytically active for the reaction of hexane at 70 °C.[10] Furthermore, Olah prepared super acids by treating metal halides with $HSO_3F$, $HSO_3CF_3$ or $CF_3COOH$ and studied their activities for the $C_6$-isomerization.[11] Gates et al. reported that a complex of $AlCl_3$ with polystyrene sulfonic acid is active for the isomerization of hexane at 85 °C.[12] Gardner presented $SbF_5-HSO_3CF_3$ supported on fluorinated alumina as an active catalyst even at ambient temperature.[13] The super acid $HF-TaF_5$ was used by Siskin et al. for the isomerization of a petroleum mixture containing hexane, benzene and cyclohexane.[14] Several patents concerning the isomerization of a pentane-hexane mixture catalyzed by Pt-impregnated H-mordenite,[15] platinum supported on chlorinated alumina[16] and super acids such as $SbF_5$ on $Al_2O_3/HF$[17] were reported.

In order to study the reactivity of very acidic surfaces, we prepared the following catalysts: $AlEtCl_2-SiO_2$, $AlEtCl_2-SiO_2-TiO_2$, $SbF_5-SiO_2$, $SbF_5-SiO_2-TiO_2$, $BF_3-SiO_2$, $BF_3-SiO_2-TiO_2$, $AlEtCl_2-$Amberlyst 15, $SbF_5-$Amberlyst 15 and $BF_3-$Amberlyst 15. The carriers were calcined at different temperatures. The catalytic properties of these systems were studied for the isomerization of hexane. The results are discussed on the basis of the

*Table 1.* Amount of metal halides remaining in the acid catalysts [in mmol g$^{-1}$].

| Catalyst | Calcination temp. [°C] | Al | Sb | B | Cl | F |
|---|---|---|---|---|---|---|
| AlEtCl$_2$–SiO$_2$ | 200 | 1.73 | | | 3.31 | |
| AlEtCl$_2$–SiO$_2$ | 400 | 1.61 | | | 2.93 | |
| AlEtCl$_2$–SiO$_2$ | 600 | 1.31 | | | 2.42 | |
| AlEtCl$_2$–SiO$_2$–TiO$_2$ | 200 | 1.38 | | | 2.79 | |
| AlEtCl$_2$–SiO$_2$–TiO$_2$ | 400 | 1.31 | | | 2.72 | |
| AlEtCl$_2$–SiO$_2$–TiO$_2$ | 600 | 1.16 | | | 2.28 | |
| SbF$_5$–SiO$_2$ | 200 | | 1.71 | | | 6.84 |
| SbF$_5$–SiO$_2$ | 400 | | 1.73 | | | 5.98 |
| SbF$_5$–SiO$_2$ | 600 | | 1.33 | | | 4.61 |
| SbF$_5$–SiO$_2$–TiO$_2$ | 200 | | 1.70 | | | 7.39 |
| SbF$_5$–SiO$_2$–TiO$_2$ | 400 | | 1.63 | | | 6.68 |
| SbF$_5$–SiO$_2$–TiO$_2$ | 600 | | 1.55 | | | 6.28 |
| BF$_3$–SiO$_2$ | 200 | | | 0.87 | | 2.01 |
| BF$_3$–SiO$_2$ | 600 | | | 0.50 | | 0.93 |
| BF$_3$–SiO$_2$–TiO$_2$ | 200 | | | 0.93 | | 2.55 |
| BF$_3$–SiO$_2$–TiO$_2$ | 600 | | | 0.78 | | 1.62 |
| AlEtCl$_2$–Amberlyst 15 | | 0.03 | | | 1.08 | |
| SbF$_5$–Amberlyst 15 | | | 1.26 | | | 5.86 |
| BF$_3$–Amberlyst 15 | | | | 0.16 | | 0.14 |

surface properties and product distributions. Very acidic catalysts can be used at low temperatures and therefore give high concentration of iso-derivatives.

Solid acid catalysts are desired because of their great advantages such as easy separation of the products from the reaction mixture, the possibility of repeated use of the catalyst and reduced corrosion problems.

## RESULTS

As shown in Table 1, the metal halide content of the catalysts decreases with increase in the calcination temperature for the metal oxides, except for the SbF$_5$–SiO$_2$ catalysts calcined at 200 and 400 °C. In these cases the amount of Sb is at the same level of about 1.72 mmol · g$^{-1}$ for each catalyst. The product distributions and the conversions for the reaction of hexane over the different types of catalysts are summarized in Tables 2 and 3 for the isomerizations carried out at 30 and 100 °C, respectively. The product mixtures consisted mostly of C$_6$-alkanes and

small amounts of isobutane, isopentane and two heptane-isomers. Usually, no significant changes in product distributions were observed after the time mentioned in the tables. This was due to deactivation of the catalysts.

Among the catalysts examined at 30 °C, only the systems with SbF$_5$ showed catalytic activity, with the highest conversion after 5−6 h of about 42.5 % for both the SbF$_5$–SiO$_2$ and SbF$_5$–SiO$_2$–TiO$_2$ catalysts calcined at 200 °C. As the calcination temperature became higher, the value of the maximum conversion was decreased for about the same reaction times, except for the SbF$_5$–SiO$_2$–TiO$_2$ system calcined at 600 °C. This catalyst showed an activity almost on the same level as observed for the system calcined at 200 °C.

The results for the isomerization at 100 °C are reported in Table 3. The conversion for the SbF$_5$-treated catalysts were not as high as when the catalysts were used at 30 °C, but it turned out that they showed the same behaviour concerning the dependence from the calcination temperature. Furthermore, the isomerization reactions at 100 °C, using SbF$_5$-based catalysts, proceeded

*Table 2.* Reaction of hexane over acid catalysts at 30 °C.

| Catalyst | Calcination temp. [°C] | Time [h] | Distribution of products [%][a] | | | | | | | | | Conversion [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | I–C4 | I–C5 | N–C6 | 2MC5 | 3MC5 | 2,3DMC4 | 2,2DMC4 | 2,2DMC5 | 3,3DMC5 | |
| AlEtCl2–SiO2 | 200 | 94 | 0 | 0 | 97.0 | 0.7 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0.10 |
| AlEtCl2–SiO2 | 400 | 92 | 0 | 0 | 97.1 | 0.6 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0 |
| AlEtCl2–SiO2 | 600 | 140 | 0 | 0 | 97.1 | 0.7 | 0.8 | 0 | 0 | 1.3 | 0.1 | 0 |
| AlEtCl2–SiO2–TiO2 | 200 | 142 | 0 | 0 | 95.6 | 1.2 | 0.6 | 0.1 | 0 | 1.0 | 1.5 | 1.6 |
| AlEtCl2–SiO2–TiO2 | 400 | 144 | 0 | 0 | 96.9 | 1.0 | 0.6 | 0.1 | 0 | 1.1 | 0.2 | 0 |
| AlEtCl2–SiO2–TiO2 | 600 | 141 | 0 | 0 | 97.0 | 0.9 | 0.7 | 0 | 0 | 1.2 | 0.2 | 0 |
| SbF5–SiO2 | 200 | 5 | 0.6 | 0.7 | 55.9 | 20.4 | 9.5 | 7.7 | 4.2 | 0.1 | 0.9 | 42.4 |
| SbF5–SiO2 | 400 | 20.5 | 0.3 | 0.3 | 71.6 | 13.7 | 6.3 | 4.9 | 1.7 | 0.1 | 1.1 | 26.2 |
| SbF5–SiO2 | 600 | 6.75 | 0 | 0 | 80.7 | 9.8 | 4.6 | 2.9 | 0.6 | 0.3 | 1.1 | 16.9 |
| | | 25 | 0 | 0.1 | 72.8 | 13.6 | 6.3 | 4.6 | 1.3 | 0.1 | 1.1 | 25.0 |
| SbF5–SiO2–TiO2 | 200 | 6 | 1.4 | 1.8 | 55.9 | 19.2 | 8.9 | 7.6 | 4.4 | 0 | 0.8 | 42.5 |
| SbF5–SiO2–TiO2 | 400 | 4.5 | 0 | 0.4 | 61.7 | 18.4 | 8.5 | 6.6 | 3.3 | 0.1 | 1.0 | 36.4 |
| | | 28 | 0[b] | 0.6 | 58.2 | 19.5 | 9.0 | 7.3 | 3.9 | 0.1 | 0.9 | 40.1 |
| SbF5–SiO2–TiO2 | 600 | 5 | 0 | 0.5 | 58.6 | 19.7 | 9.1 | 7.2 | 3.8 | 0.1 | 1.0 | 39.7 |
| BF3–SiO2 | 200 | 50 | 0 | 0 | 96.4 | 1.0 | 1.0 | 0.2 | 0 | 1.3 | 0.1 | 0.7 |
| BF3–SiO2 | 600 | 289 | 0 | 0 | 97.0 | 0.7 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0.0 |
| BF3–SiO2–TiO2 | 200 | 50.5 | 0 | 0 | 96.7 | 0.9 | 0.9 | 0.1 | 0 | 1.3 | 0.1 | 0.4 |
| BF3–SiO2–TiO2 | 600 | 289 | 0 | 0 | 97.1 | 0.6 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0 |
| AlEtCl2–Amberlyst 15 | | 142.5 | 0 | 0 | 97.0 | 0.9 | 0.6 | 0.1 | 0 | 1.2 | 0.2 | 0.1 |
| SbF5–Amberlyst 15 | | 6.5 | 0.2 | 0.2 | 84.8 | 7.0 | 3.3 | 2.9 | 0.5 | 0.1 | 1.1 | 12.7 |
| BF3–Amberlyst 15 | | 51 | 0 | 0 | 96.5 | 0.9 | 0.9 | 0.2 | 0.1 | 1.3 | 0.1 | 0.6 |

[a] I–C4: isobutane; I–C5: isopentane; N–C6: n-hexane; 2MC5: 2-methylpentane; 3MC5: 3-methylpentane; 2,3DMC4: 2,3-dimethylbutane; 2,2DMC4: 2,2-dimethylbutane; 2,2DMC5: 2,2-dimethylpentane; 3,3DMC5: 3,3-dimethylpentane. [b] n-butane: 0.5 %.

*Table 3.* Reaction of hexane over acid catalysts at 100 °C.

| Catalyst | Calcination temp. [°C] | Time [h] | Distribution of products [%][a] | | | | | | | | | Conversion [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | I–C4 | I–C5 | N–C6 | 2MC5 | 3MC5 | 2,3DMC4 | 2,2DMC4 | 2,2DMC5 | 3,3DMC5 | |
| AlEtCl₂–SiO₂ | 200 | 218 | 1.4 | 1.3 | 39.7 | 27.6 | 15.0 | 9.8 | 4.5 | 0.2 | 0.4 | 59.2 |
| AlEtCl₂–SiO₂ | 400 | 312 | 0.6 | 0.6 | 49.0 | 24.4 | 13.4 | 8.4 | 2.8 | 0.2 | 0.6 | 49.5 |
| AlEtCl₂–SiO₂ | 600 | 359 | 0.3 | 0.3 | 65.3 | 17.0 | 9.3 | 5.6 | 1.2 | 0.3 | 0.7 | 32.7 |
| AlEtCl₂–SiO₂–TiO₂ | 200 | 161.5 | 0.5 | 0.4 | 62.6 | 18.2 | 9.9 | 6.0 | 1.6 | 0.2 | 0.6 | 35.6 |
| AlEtCl₂–SiO₂–TiO₂ | 400 | 195 | 0.3 | 0.2 | 74.9 | 12.2 | 6.7 | 4.0 | 0.7 | 0.2 | 0.7 | 22.8 |
| AlEtCl₂–SiO₂–TiO₂ | 600 | 167.5 | 0.2 | 0.1 | 84.2 | 7.7 | 4.2 | 2.3 | 0.3 | 0.2 | 0.8 | 13.3 |
| SbF₅–SiO₂ | 200 | 0.5 | 0.3 | 0.2 | 76.3 | 11.3 | 6.1 | 3.9 | 0.8 | 0.2 | 0.8 | 21.4 |
| SbF₅–SiO₂ | 400 | 1 | 0 | 0.1 | 85.0 | 7.1 | 3.9 | 2.4 | 0.3 | 0.2 | 1.0 | 12.5 |
| SbF₅–SiO₂ | 600 | 1 | 0.1 | 0.1 | 86.4 | 6.4 | 3.4 | 2.1 | 0.3 | 0.3 | 0.9 | 11.0 |
| SbF₅–SiO₂–TiO₂ | 200 | 0.75 | 0.5 | 0.5 | 74.0 | 12.1 | 6.5 | 4.3 | 1.1 | 0.2 | 0.8 | 23.8 |
| SbF₅–SiO₂–TiO₂ | 400 | 0.75 | 0 | 0.5 | 77.1 | 10.7 | 5.6 | 3.7 | 1.3 | 0.2 | 0.9 | 20.6 |
| SbF₅–SiO₂–TiO₂ | 600 | 0.75 | 0.2 | 0.2 | 82.9 | 7.9 | 4.3 | 2.6 | 0.8 | 0.3 | 0.8 | 14.5 |
| BF₃–SiO₂ | 200 | 290 | 0 | 0 | 97.0 | 0.6 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0 |
| BF₃–SiO₂ | 600 | 187 | 0 | 0 | 97.1 | 0.6 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0 |
| BF₃–SiO₂–TiO₂ | 200 | 290.5 | 0.2 | 0 | 96.9 | 0.6 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0 |
| BF₃–SiO₂–TiO₂ | 600 | 163.5 | 0 | 0 | 97.1 | 0.6 | 0.8 | 0.1 | 0 | 1.3 | 0.1 | 0 |
| AlEtCl₂–Amberlyst 15 | | 186 | 0 | 0 | 96.8 | 0.8 | 0.9 | 0.1 | 0 | 1.3 | 0.1 | 0.2 |
| SbF₅–Amberlyst 15 | | 0.5 | 0.3 | 0.2 | 92.5 | 3.0 | 1.6 | 1.0 | 0.2 | 0.6 | 0.6 | 4.7 |

[a] I–C4: isobutane; I–C5: isopentane; N–C6: n-hexane; 2MC5: 2-methylpentane; 3MC5: 3-methylpentane; 2,3DMC4: 2,3-dimethylbutane; 2,2DMC4: 2,2-dimethylbutane; 2,2DMC5: 2,2-dimethylpentane; 3,3DMC5: 3,3-dimethylpentane.

faster than those at 30 °C. The maximum conversion values were reached already after 0.5–1 h.

In opposition to the results obtained for the isomerization at 30 °C, the AlEtCl₂ systems with silica and silica-titania as carriers were found to be active at 100 °C, including the system giving the highest conversion observed in this study, the AlEtCl₂–SiO₂ catalyst with a conversion of nearly 60 %. On the other hand, the conversions found for the AlEtCl₂-treated catalysts were first obtained after several days reaction time, i.e. the induction period is very long. A shortening of the induction period was obtained by using a small amount (4.5 $\mu$l) of isopropyl chloride as a promotor in addition to the AlEtCl₂–SiO₂ catalyst. The resulting effect was small and the conversion observed was not as high as that obtained for the reaction without the promotor. The preparation conditions of the metal oxides in the cases of the AlEtCl₂-based catalysts also affected the catalytic behaviour, i.e. decreased activity with increasing calcination temperature.

The binary component metal oxide systems (SiO₂–TiO₂) were the most effective catalysts among the SbF₅-based ones, whereas the opposite findings were obtained for the AlEtCl₂-based catalysts, i.e. the single component metal oxide systems AlEtCl₂–SiO₂ were more active at 100 °C than the AlEtCl₂–SiO₂–TiO₂ catalysts.

Also at the reaction temperature of 100 °C no activity was found, neither for the BF₃-treated catalysts nor for the system AlEtCl₂-Amberlyst 15.

The SbF₅-Amberlyst 15 systems showed little activity at 30 °C as well as at 100 °C.

At the maximum conversion, the selectivities of the active acid catalysts for the skeletal isomerization were in most cases better than 91 %. One exception was registrated for the system SbF₅–SiO₂–TiO₂ (200 °C calc. temp.) at 30 °C with a selectivity of 89 %.

Finally, it should be emphasized that the amounts of the produced iso-hexanes in all cases were found to be in the following manner: 2-methylpentane>3-methylpentane>2,3-dimethylbutane>2,2-dimethylbutane.

## DISCUSSION

In the present work, the maximum conversions of hexane to the corresponding branched derivatives were found to be affected by factors caused by the preparation procedures of the catalysts. From the details examined in this study, the temperature at which the metal oxides were calcined exhibited the greatest effect. To obtain a high maximum conversion to isohexanes, a low calcination temperature is desirable. Furthermore, it is evident that SbF₅ was the most effective metal halide among the reagents with which metal oxides were treated. On treatment with SbF₅, the metal oxides SiO₂ and SiO₂–TiO₂ and the Amberlyst 15 became active for the isomerization of hexane. Finally, comparison of Tables 2 and 3 with Table 1 reveals that the maximum conversion increases with the increase of the content of metal halide in the catalysts. Since the catalytic activity became smaller when the metal oxide support had been precalcined at higher temperature, the presence of hydroxyl groups on the metal oxide seems to be necessary to form the active sites by treatment with the metal halide. It is well known that an increase in the calcination temperature leads to a decrease of the number of OH groups. In the catalyst, SbF₅ probably interacts with the surface hydroxyl groups. The structure of the acidic sites on SbF₅–SiO₂ may be drawn as follows:



Scheme 1.
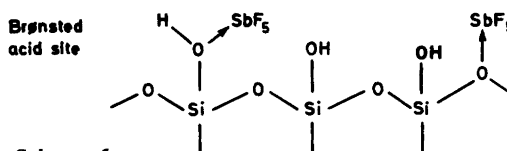
The coordination of SbF₅ to the hydroxyl groups will increase the acid strength of the OH groups (Brönsted acid sites). Accordingly, we postulate that the activity increases with increased numbers of hydroxyl groups and increased amounts of metal halides. This means that a low pretreatment temperature for the metal oxides is desired for high conversions. Hattori et al.[6] reported that the metal halide reacted with the surface hydroxyl groups at higher temperatures 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 line with corresponding investigations made by our group concerning the anchoring of TiCl₄ on silica.[18]

The type of metal oxide (single or binary

component system) used for the SbF$_5$-treated catalysts strongly affected the catalytic activity. The SbF$_5$–SiO$_2$–TiO$_2$ systems were more active than the SbF$_5$–SiO$_2$ ones, *i.e.* the acid strength of the binary system seems to be somewhat higher than that of the single component catalyst. Our findings are in agreement with the results reported by Hattori *et al.*[6] for the reaction of butane over SbF$_5$–SiO$_2$ and SbF$_5$–SiO$_2$–TiO$_2$ catalysts, although the measured Hammett $H_o$-values for the two catalysts were found to be in the same range of about $-13.16 \geqslant H_o > -13.75$.[6,19] However, one should take into account that very small changes of the acid strength of these catalysts cannot be registrated by the colour change method using Hammett indicators.

Since the AlEtCl$_2$-based catalysts first became active after several days at 100 °C, it may be concluded that their use from an industrial point of view is not desired. The observed shortening of the induction period for the AlEtCl$_2$–SiO$_2$ catalyst by the use of isopropyl chloride as a promotor is in agreement with the results reported by Franck *et al.*[20] This group succeeded in the isomerization of n-pentane catalyzed by ethylaluminium sesquichloride anchored on a platinum-impregnated alumina with HCl as a promotor. On the basis of our results concerning the relationship between the preparation conditions and the activity of the catalysts, we observed the same catalytic behaviour also for the AlEtCl$_2$-systems.

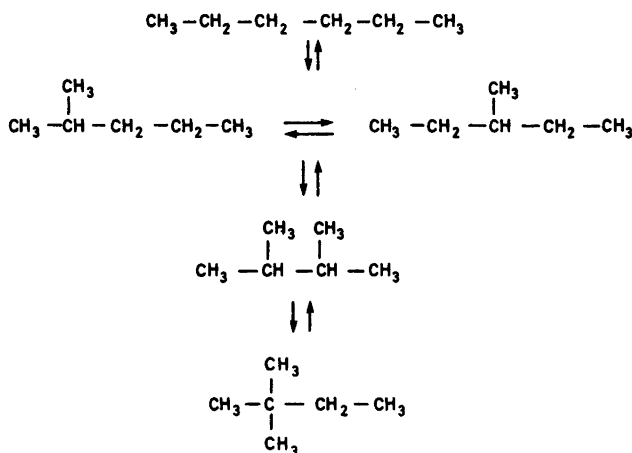The low conversions at 100 °C for the SbF$_5$-treated catalysts compared with the values obtained at 30 °C and the constant product distributions observed already after 0.5–1 h at 100 °C, were referred to a short lifetime of the catalysts at this temperature, *i.e.* the catalysts were presumably deactivated after this time. The most likely explanation was that SbF$_5$-supported catalysts were very thermally unstable. The active SbF$_5$-species reacted further with the surface to give an inactive catalyst.

Hexane isomerization occurs by consecutive reversible reactions, as outlined in the following scheme:[4]

Since our product distributions were observed to be far from the equilibrium concentration, the distribution of the hexane isomers, reported in Tables 2 and 3, were in agreement with the proposed mechanism for the C$_6$-isomerization.

## CONCLUSION

From the examination of our results it was concluded that the use of the SbF$_5$-based solid super acids provided the highest conversions at relatively low reaction temperature. The deactivation properties and lifetimes of the catalysts should be improved before practical use in industry is recommended. It is shown that the temperature is an important factor in the product distribution control, since the most highly branched hexane isomers, the high octane dimethylbutanes, are thermodynamically favored at low isomerization temperatures. Low temperatures also serve to minimize side reactions such as alkene formation and cracking reactions.[14]

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

$$
\begin{array}{c}
CH_3 \\
|\\
CH_3-CH-CH_2-CH_2-CH_3
\end{array}
\quad \rightleftharpoons \quad
\begin{array}{c}
CH_3 \\
|\\
CH_3-CH_2-CH-CH_2-CH_3
\end{array}
$$

$$
\begin{array}{c}
CH_3 \quad CH_3 \\
|\qquad| \\
CH_3-CH-CH-CH_3
\end{array}
$$

$$
\begin{array}{c}
CH_3 \\
|\\
CH_3-C-CH_2-CH_3 \\
|\\
CH_3
\end{array}
$$

*Scheme 2.*

## EXPERIMENTAL

Silica (35−70 mesh) and Amberlyst 15 (beads of a macroporous, sulfonated polystyrene-divinyl-benzene) were obtained from standard commercial sources (Merck and Fluka, respectively). The silica was treated with conc. HCL for 4 h, followed by washing with deionized water and drying at room temperature under vacuum for 60 h. Amberlyst 15 was washed with deionized water and MeOH before drying at 120 °C, under vacuum for 72 h. The $SiO_2-TiO_2$ carrier was prepared as follows: A mixture of 1 ml 5 N $TiCl_4$/g $SiO_2$ in n-heptane was stirred for 5 h. After evaporation of the solvent and evacuation for 96 h the mixture was exposed to water vapor for 24 h at 125 °C and afterwards for 4 h at 200 °C. Both the silica and silica-titania were divided into three portions and calcined at 200, 400 and 600 °C, respectively, for 18 h in $N_2$-atmosphere before treatment with the metal halides.

*AlEtCl₂-treated catalysts.* The metal oxides (5 g) and Amberlyst 15 (8 g) were treated with a solution of n-heptane (20 ml) and 50 % $AlEtCl_2$ in n-heptane (3 ml and 8 ml, respectively). After two hours, the solution was filtrated, and the catalyst was washed with n-heptane and phenyl chloride. Finally, the catalyst was dried under vacuum for 23 h at room temperature.

*SbF₅-treated catalysts.* The carriers (5 g) were exposed to the vapor of $SbF_5$ for 4 h, followed by evacuation for 144 h at room temperature.

*BF₃-treated catalysts.* The catalysts were prepared by contacting the carriers (about 6 g) with vapor of $BF_3$ for 40 min and evacuating for about 120 h at room temperature.

The reactions were carried out in 3 ml glass micro reaction vessels (Supelco, Inc.), equipped with teflon constructed Mininert valves. 2 ml n-hexane (Merck, 97.1 % purity) were allowed to react over 100 mg of the catalyst. 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 15 min. The percentage conversions were obtained by measuring peak areas (corrected).

## REFERENCES

1. Brouwer, D. M. *Rec. Trav. Chim. Pays-Bas 87* (1968) 1435; *Chem. Ind.* (1970) 1459.
2. Brouwer, D. M. and Oelderik, J. M. *Rec. Trav. Chim. Pays-Bas 87* (1968) 721.
3. Brouwer, D. M. and Hogeveen, H. *Prog. Phys. Org. Chem. 9* (1972) 179.
4. Bonifay, R., Torck, B. and Hellin, M. *Bull. Soc. Chim. Fr.* (1977) 1057.
5. Brunel, D., Itier, J., Commeyras, A., Phan Tan Luu, R. and Mathieu, D. *Bull. Soc. Chim. Fr.* (1979) 249.
6. Hattori, H., Takahashi, O., Takagi, M. and Tanabe, K. *J. Catal. 68* (1981) 132.
7. Takahashi, O. and Hattori, H. *J. Catal. 68* (1981) 144.
8. Heinermann, J. J. L. and Gaaf, J. *J. Mol. Catal. 11* (1981) 215.
9. Krzywicki, A., Marczewski, M. and Malinowski, S. *React. Kint. Catal. Lett. 8* (1978) 25.
10. Olah, G. A. *US Pat.* 4 116 880 (1978).
11. Olah, G. A. *US Pat.* 3 766 286 (1973).
12. Magnotta, V. L. and Gates, B. C. *J. Catal. 46* (1977) 266.
13. Gardner, L. E. *US Pat.* 3 878 261 (1975).
14. Siskin, M., Chludzinski, G. R., Hulme, R., Porcelli, J. J. and Tyler, W. E., III *Ind. Eng. Chem. Prod. Res. Dev. 19* (1980) 379.
15. Shell Internationale Research Maatschappij N. V. *Brit. Pat.* 1 012 206 (1965).
16. Goble, A. G. and Haresnape, J. N. *Brit. Pat.* 953 187 (1964).
17. Crathorne, E. A., Howell, J. V. and Pitkethly, R. C. *US Pat.* 3 975 299 (1976).
18. Riis, T., Dahl, I. M. and Ellestad, O. H. *J. Mol. Catal. 18* (1983) 203.
19. 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.
20. Franck, J. P., Le Page, J. F. and Roumegous, A. *Proceedings of the 7th International Congress on Catalysis, Part B,* Elsevier, Amsterdam 1981, p. 1018.