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LOW TEMPERATURE ISOMERIZATION OF PARAFFINS OVER ALUMINA TREATED WITH CF_3Cl

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Paraffins such as butane, pentane, and hexane were isomerized, at temperatures as low as 0°C, over Al_2O_3 treated with CF_3Cl. The isomerizations were promoted by strong acid sites having H_o values of $-13.75 \geq H_o > -14.52$, which were formed on the treated surface.

Since paraffin is extremely stable, its isomerization and disproportionation hardly proceed even in the presence of typical strong acid catalysts. Only markedly strong acids, the so-called super strong acids or "magic acids" can promote these reactions under relatively mild reaction conditions.[1-2] In order to utilize paraffin enriched petroleum, the isomerization reaction is now attracting more interest.

We have observed that Al_2O_3-Cr_2O_3 treated with chlorofluoromethanes, especially CF_3Cl, promoted CH_3OH conversion into olefins and that the Al component was essential to the catalytic activity for conversion.[3] These facts suggested the presence of strong acid sites on Al_2O_3 treated with CF_3Cl, because the conversion can be promoted only by remarkably strong acid sites.[4] Hence, the catalytic activity of Al_2O_3 treated with CF_3Cl in the paraffin isomerization was examined.

Alumina was prepared from aluminum isopropoxide through hydroxide, and was heat-treated at 450-700°C in air. Just before use as a catalyst, the oxide was fabricated to granules of 0.5-1.0 mm diameter and then submitted to the surface treatment with 54 Torr of CF_3Cl at 420°C for 30 min in a circulation reactor (volume: 320 ml).

The paraffin isomerization was carried out in the circulation system, mainly

at 0°C. The products were analyzed by gas chromatography using a 7m-column packed with VZ-7.

The compositions of the surface layer of Al_2O_3 treated with CF_3Cl were determined by XPS using a Shimadzu ESCA-750 appratus. The spectra were measured with Mg-Kα radiation. Surface area and crystallinity of the Al_2O_3 before and after treatment were determined by means of N_2 adsorption at -196°C and X-ray diffraction, respectively. The acid strength was determined by the indicator adsorption method using sulfuryl chloride as a solvent.[5)]

The percentage conversions of pentane at 0°C are shown in Fig.1. The numbers in parentheses show the heat-treatment temperature (°C) of Al_2O_3 before CF_3Cl-treatment. The catalytic activity of CF_3Cl-treated Al_2O_3 was highly dependent on this temperature.

As is shown in Fig.1, the amount of isopentane increased linearly with reaction time and attained a maximum after a few hours; at this time the isopentane was further converted into isobutane and isohexane. (The amounts of isobutane and isohexane are shown only for the reaction over CF_3Cl-treated Al_2O_3 (600).) The conversion of isopentane into isobutane and isohexane was confirmed more directly by the reaction of isopentane over CF_3Cl-treated Al_2O_3(600)(Fig.2). These results suggest that successive reactions such as

Pentane ⟶ Isopentane ⟶ Isobutane + Isohexane

might take place at a temperature as low as 0°C in the pentane conversion over CF_3Cl-treated Al_2O_3.

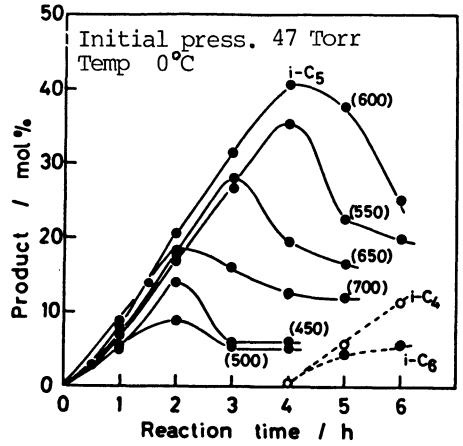

Fig.1. Pentane.
------: for Al_2O_3(600) treated with CF_3Cl.

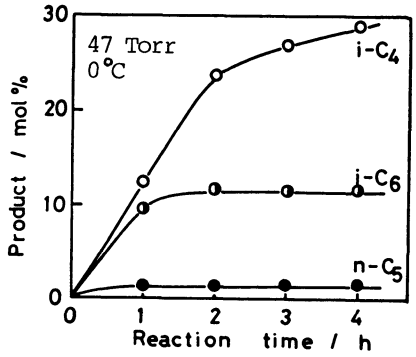

Fig.2. Isopentane.

As Fig.3 shows, the isomerization of hexane proceeded more easily than that of pentane over CF_3Cl-treated Al_2O_3(600). For reaction times longer than 3 h, considerable amounts of isopentane and isobutane formed together with isohexane. The absence of isoheptane may be due to the fact that longer chain paraffins of branched structure should be less stable, and be converted into other shorter chain paraffins. Butane isomerization was promoted by CF_3Cl-treated Al_2O_3(600) at 0°C(Fig.4). Although the conversion at 0°C was far less than those of pentane and hexane, it became significantly large as the reaction temperature was elevated to 25°C.

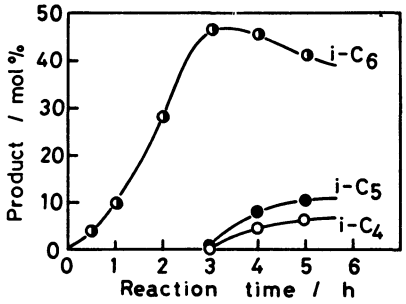

Fig.3. Hexane.

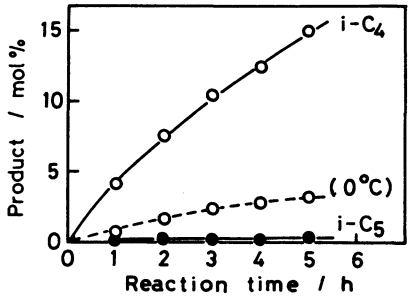

Fig.4 Butane.

Reaction temperature: 0°C for Fig.3; 25°C for Fig.4 (except for indicated)
Initial press.: 47 Torr for Figs.3 and 4.

The determination of acid strength showed that strong acid sites having the H_o values of

$$-13.75 \geq H_o > 14.52$$

were formed on the surface of Al_2O_3 by the CF_3Cl-treatment at 420°C. The specific surface area of Al_2O_3 changed on heat-treatment at temperatures of 500 to 700°C, but did not change further on successive CF_3Cl-treatment at 420°C, as is shown below:

Heat-treatment temperature(°C)	500	600	650	700
Specific surface area(m^2/g)				
before CF_3Cl-treatment	247	226	216	209
after CF_3Cl-treatment	244	225	213	201

As the XPS patterns(Fig.5) show, the peak position of the O_{1s} for Al_2O_3 treated with CF_3Cl coincided with that for Al_2O_3 before CF_3Cl-treatment, and the peak position of the Al_{2p} for treated Al_2O_3 was very close to that for untreated Al_2O_3, being far from that of AlF_3. These facts suggested that the Al_2O_3 tructure was retained after the CF_3Cl-treatment. On the other hand, the position

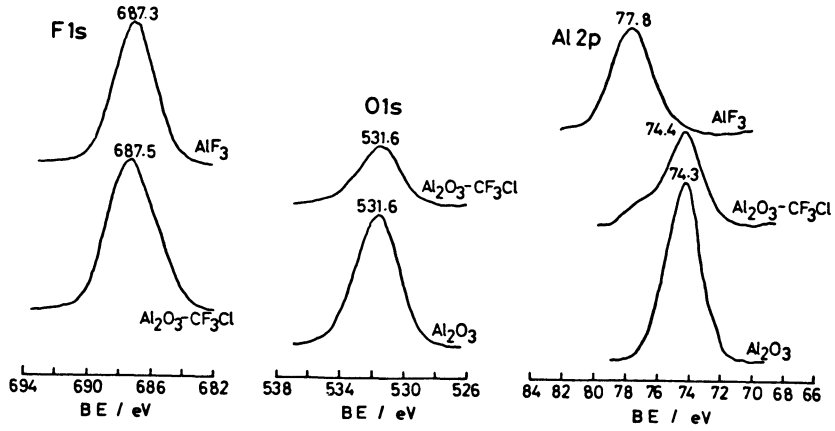

Fig.5. XPS patterns for Al_2O_3 before and after treatment with CF_3Cl, and for AlF_3.

of the F_{1s} peak of CF_3Cl-treated Al_2O_3 almost coincided with that of AlF_3. An Al-F bond similar to that existing in stable or crystalline AlF_3 may be formed on the surface of CF_3Cl-treated Al_2O_3. These XPS results can be summarized as follows: the F atoms which were introduced by CF_3Cl bonded to Al atoms(or ions) of Al_2O_3, so that Al fluoride was formed on the Al_2O_3; however, stable AlF_3 was not formed and the active or amorphous(or less-crystallized)Al_2O_3 structure was retained unless the CF_3Cl-treatment was carried out at temperatures higher than 450°C. The fact that stable or crystalline AlF_3 was essentially absent on the surface of Al_2O_3 treated with CF_3Cl at temperatures lower than 450°C was further confirmed by XRD analysis. Thus, CF_3Cl-treatment at temperatures higher than 450°C must be avoided because of formation of crystalline or inactive AlF_3. On the other hand, CF_3Cl-treatment temperatures higher than 400°C were essential to convert Al_2O_3 into catalytically active species for paraffin isomerizations. Hence, Al_2O_3 must be treated with CF_3Cl over a relatively narrow temperature range around 420°C to obtain sufficiently high catalytic activity for paraffin isomerization reactions.

References

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