## Alumina Solid Lewis Superacid: Activated Benzene and Isomerization of Alkanes on Aluminas Chlorinated at High Temperature

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Alumina solid Lewis superacids, prepared by high temperature chlorination of  $\gamma$ -alumina, activate benzene to yield a charge-transfer  $\pi$ -complex and selectively isomerize cyclohexane, pentane, and butane to methylcyclopentane, 2-methylbutane, and 2-methylpropane, respectively, at 303 K.

The preparation of solid Lewis acid catalysts for use instead of homogeneous Lewis acids is industrially important. We have succeeded in the preparation of alumina superacids with Lewis acid centres and  $H_{\circ} \leq -14.52$  by high temperature treatment in chlorine.<sup>1</sup> The alumina used was JRC-ALO-4 in the  $\gamma$ -form (174 m<sup>2</sup> g<sup>-1</sup>; Japan Reference Catalyst). A self-supported disc and the powder under 60 µm $\varphi$  were employed for i.r. and u.v.-vis. spectroscopic measurements, respectively. For low alkane isomerization particles of 0.5–1.0 mm $\varphi$  were also used. These samples were treated in chlorine (10 kPa, 1073 K) for 1 h and then outgassed.<sup>1</sup> All the chlorinated aluminas were handled *in vacuo*.

On adsorption of benzene at room temperature, the colour of the chlorinated alumina changed from white to light yellow. The u.v.-vis. spectrum of the adsorbed benzene showed  $\lambda_{max}$ . at 294 nm and coincided with that of benzene co-ordinated with aluminium trichloride. This indicated that a charge-transfer  $\pi$ -complex was formed between a strong Lewis acid centre and a benzene molecule.<sup>2.3</sup> On coadsorption of propene and benzene on the alumina, a doublet band consisting of peaks at 1362 and 1382 cm<sup>-1</sup> assigned to the symmetrical deformation vibrations of the isopropyl group

and an intense  $1605 \text{ cm}^{-1}$  peak characteristic of the aromatic ring vibration of monosubstituted benzene were recorded, demonstrating the formation of isopropylbenzene.

The isomerization of alkanes was carried out using a conventional circular reactor. Cyclohexane was isomerized to methylcyclopentane only and butane to 2-methylpropane with 100% selectivity (Table 1). The skeletal isomerisations took place selectively below 313 K, but above this temperature cracking reactions occurred preferentially. Pentane was isomerized to 2-methylbutane with 95.6% selectivity, the minor product being 2-methylpropane. On exposure to air after the reaction, the colour of the catalyst surface changed from white to light yellow, which appears to indicate that the cracked species, *i.e.*, CH<sub>2</sub>, had been deposited on the surface. Hattori et al. reported that the isomerization of alkanes took place at the Lewis acid centres of a  $SbF_5/Al_2O_3-SiO_2$ superacid catalyst.<sup>4</sup> The order cyclohexane > pentane > butane for alkane conversion in the present work agrees with that observed for SbF<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Chlorination showed maximum effect on the isomerizations conducted at 1223 K (Table 1). The structure of the chlorinated aluminas was almost  $\theta$ -phase<sup>5</sup> and the surface areas were 113–101 m<sup>2</sup> g<sup>-1</sup>.

Table 1. Conversions and product compositions in the isomerization of cyclohexane, pentane and butane on the ALO-4 chlorinated at different temperatures.<sup>a</sup>

| Chlorination<br>temperature/<br>K | Cyclohexane |                                       | Butane      |                                      | Pentane     |                             |                 |                  |
|-----------------------------------|-------------|---------------------------------------|-------------|--------------------------------------|-------------|-----------------------------|-----------------|------------------|
|                                   | Conv./<br>% | Composition/<br>%<br>MCP <sup>b</sup> | Conv /      | Composition/<br>%<br>C4 <sup>i</sup> | Conv./<br>% | Composition/%               |                 |                  |
|                                   |             |                                       | %           |                                      |             | C <sub>5</sub> <sup>i</sup> | C4 <sup>i</sup> | 2MP <sup>c</sup> |
| 1073<br>1223                      | 9.6<br>14.4 | 100<br>100                            | 4.8<br>10.2 | 100<br>100                           | 6.0<br>13.0 | 95.6<br>96.5                | 4.4<br>2.7      | 0.0<br>0.8       |
| 1323                              | 8.3         | 100                                   | 6.2         | 100                                  | 5.2         | 95.0                        | 5.0             | 0.0              |

<sup>a</sup> Catalyst weight 0.25 g; alkane partial pressure 5.3 kPa; reaction temperature 303 K; reaction time 2 h. <sup>b</sup> Methylcyclopentane. <sup>c</sup> 2-Methyl-pentane.

The use of aluminium trichloride in the butane isomerization yielded, for example, propane and pentanes as byproducts,<sup>6</sup> but the high temperature chlorinated aluminas produced 2-methylpropane only. The aluminas are thus valid as solid catalysts for alkane isomerization, to be used instead of homogeneous Lewis acid catalysts. Further, the occurrence of low alkane isomerization around room temperature strongly indicates that the chlorinated aluminas are solid Lewis superacids.<sup>7</sup>

Received, 25th January 1989; Com. 9/00407F

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