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## Hydrogenation over Alumina

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**Summary** Commercial  $\gamma$ -aluminas which contain traces of iron can, after alkali treatment at 373 K, dissociate molecular hydrogen and catalyse the hydrogenation of pent-1-ene and buta-1,3-diene at ambient temperature and above.

$\gamma$ -ALUMINA is unable to dissociate molecular hydrogen, and therefore to act as a hydrogenation catalyst, below about 773 K.<sup>1</sup> However, its activity in these respects is increased by the introduction of iron impurity centres,<sup>2</sup> high energy or 'strained' sites<sup>3</sup> produced by dehydroxylation above about 773 K,<sup>3,4</sup> or surface defect centres produced by ionising radiation.<sup>5</sup> We have found that mild alkali treatment of commercial  $\gamma$ -aluminas produces materials possessing these adsorptive and catalytic properties. For example, 18 g of commercial  $\gamma$ -alumina [Degussa, (surface area 117 m<sup>2</sup> g<sup>-2</sup>; [Fe] 2000 p.p.m.) or I.C.I. 13/1 (surface area 150 m<sup>2</sup> g<sup>-1</sup>; [Fe] 50 p.p.m.)] was refluxed in 200 cm<sup>3</sup> of a 1M solution of sodium acetate for up to 26 h. Samples were extracted at various times and filtered, washed in 1300 cm<sup>3</sup> of boiling distilled water and dried in air at 393 K for 16 h. Other alkali solutions successfully used include sodium and potassium hydroxides.

Some results and experimental details for pent-1-ene hydrogenation and isomerisation are shown in the Table. The aluminas showed activities which were dependent upon the length of treatment and which did not decrease with time. Maximum hydrogenation activity occurred after longer times of alkali treatment than did the maximum in isomerisation activity. These aluminas catalysed the hydrogenation of pent-1-ene and buta-1,3-diene (to butene)

at and above ambient temperature. The low activation energies (9.9 and 15.0 kJ mol<sup>-1</sup> respectively) between 297 and 463 K may indicate diffusion limitation of the reactions.

X-ray diffraction, transmission electron microscopy, and differential thermal analysis showed that the mild alkali treatment for 25 h converted less than 30% of the  $\gamma$ -alumina to boehmite [AlO(OH)] and pseudo-boehmite. Pure  $\gamma$ -alumina, boehmite and pseudo-boehmite taken separately were found to be inactive in the hydrogenation-isomerisation of pent-1-ene. No change in iron concentration on alkali treatment was detected by atomic absorption spectroscopy, but e.s.r. showed that the fractions of iron in various states in alumina were affected.

TABLE. The activities of some aluminas prepared by sodium acetate treatment of I.C.I. 13/1  $\gamma$ -alumina in the hydrogenation and isomerisation of pent-1-ene

Sample	Length of sodium acetate treatment/h	Product composition <sup>a</sup>	
		% pentane	% <i>trans</i> - and <i>cis</i> -pent-2-ene
1	3	30	70
2	7	42	58
3	11	48	52
4	25	21	0
5	26	17	0

<sup>a</sup> Average conversions (0.2 g catalyst, 373 K, pent-1-ene 161 ± 7 N m<sup>-2</sup>, hydrogen 101 kN m<sup>-2</sup>, flow rate 10 cm<sup>3</sup> min<sup>-1</sup>) measured in a continuous flow reactor after 60 minutes.

Activity for pent-1-ene hydrogenation was unaffected by O<sub>2</sub>, only temporarily decreased by CO and C<sub>2</sub>H<sub>2</sub>, but increased by steam treatment; however, HCl poisoned the catalysts. Approximately the same quantities of HCl,

whether added as such or formed by thermal decomposition of  $\text{HAuCl}_4$  at 393 K, were needed to poison completely alumina prepared by treatment of Degussa  $\gamma$ -alumina with sodium acetate solution for 18 h: values were  $1.22 \times 10^{20}$  and  $1.06 \times 10^{20}$  molecules  $\text{g}^{-1}$  respectively. Assuming that each HCl molecule poisons one active site, their concentration is about two-thirds of that of surface  $-\text{OH}$  groups ( $1.65 \times 10^{20} \text{ g}^{-1}$ ) as determined by tritium retention analysis.<sup>8</sup>

We believe the conversion of  $\gamma$ -alumina into boehmite occurs by a solution-deposition mechanism. Deposition of the first layer of boehmite converts half the surface  $-\text{OH}$  groups into Lewis-acid sites, analogous to those in silica-alumina, where they are known<sup>6</sup> to adsorb alkenes. This ratio of active sites to  $-\text{OH}$  groups is in reasonable

agreement with that observed experimentally. Such sites could be poisoned by HCl. Nevertheless, a catalyst which had been poisoned completely by HCl remained capable of initiating hydrogen spillover<sup>7</sup> to tungsten trioxide at 543 K. Therefore the alkali treatment generates two types of site on the alumina surface; one possibly an 'iron' site which is capable of dissociating molecular hydrogen, and the other an 'alumina' site, possibly a Lewis acid site, which can adsorb the unsaturated hydrocarbon. Although the exact nature of these sites is as yet uncertain, it seems likely that hydrogenation involves hydrogen migration or spillover between the two.

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