New Design of Highly Active, Paired Chromium Structures on Solid Surfaces for Propene Hydrogenation

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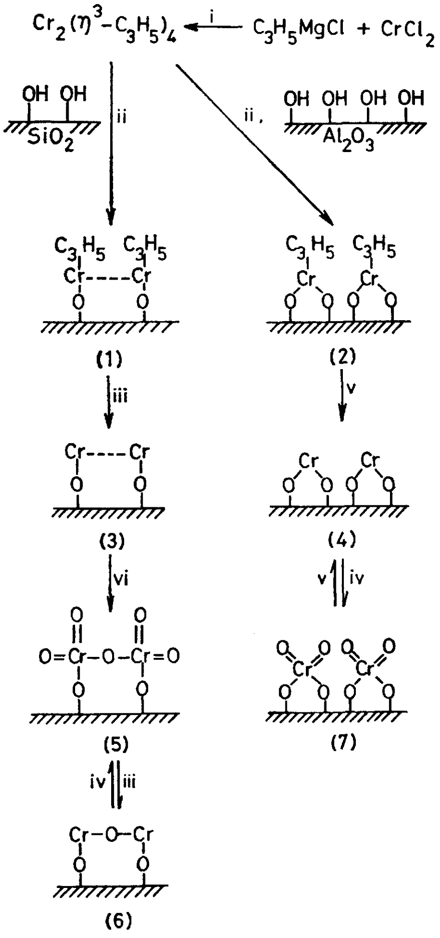
Summary Well defined 'paired' chromium species in various oxidation states on silica or alumina have been designed and studied to find the structural factors responsible for their excellent catalysis of propene hydrogenation at 195—263 K.

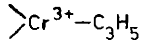
ALTHOUGH it is in general difficult to create a well defined molecular structure on ill defined, heterogeneous surfaces of inorganic oxides, it has been demonstrated that fixed 'single Mo' and 'paired Mo_2' catalysts act as well defined solid catalysts with spectroscopically and catalytically uniform reaction sites.[1] We now report the design of new, fixed 'paired Cr_2' catalysts and surface structures of active sites for propene hydrogenation.

The fixed paired Cr_2 catalysts were prepared using the reaction between $Cr_2(\eta^3\text{-}C_3H_5)_4$ and the surface protonic OH groups of SiO_2 or Al_2O_3. $Cr_2(\eta^3\text{-}C_3H_5)_4$, with a Cr–Cr bond distance of 197 pm,[2] was purified by pentane extraction and two recrystallizations at 193 K under high-purity Ar(99·9995%). All catalyst preparations were carried out under a flow of high-purity Ar or *in vacuo* (base pressure: $1{\cdot}33 \times 10^{-3}$ Pa). The Cr-fixing reaction at 273 K took place readily to form the surface complex (**1**) [SiO_2 (510 m^2/g)] or the complex (**2**) [Al_2O_3(190 m^2/g)], in the following synthesis scheme, when the numbers of the OH groups of SiO_2 and Al_2O_3 were controlled to be 1·3 and 2·6 OH/nm^2, respectively. The amounts of chromium thus fixed were determined to be 0·52 wt% (Cr/SiO_2) and 0·49 wt% (Cr/Al_2O_3) by chemical analysis.



SCHEME. Reagents and conditions: i, 253 K, 5 h, tetrahydrofuran (THF); 293 K, 3 h, THF; 0·5 h, *h*ν; 293 K, pentane; 195 K, recryst.; 293 K, pentane, ii, 273 K, iii, 860 K, H_2, iv, 773 K, O_2, v, 870 K, H_2, vi, 823 K, O_2.

The surface structures, (**1**)—(**7**), of the fixed Cr_2 catalysts were characterised spectroscopically (i.r., u.v. diffuse reflection, e.s.r., and photoluminescence), volumetrically, and by temperature programmed hydrogenolysis (t.p.h.). The C–C stretching frequency (1563 cm^{-1}) of the complex (**2**), different from that of $Cr(\eta^3\text{-}C_3H_5)_4$,[3] indicated that the allyl ligands were of the η^2-type. The dependence of the e.s.r. peak intensity (g $2{\cdot}13_5$, ΔH 1300 G) of (**2**) upon temperature suggested a weak, direct, exchange interaction between two adjacent Cr^{3+} ions; a small quantity of isolated $>Cr^{3+}\text{–}C_3H_5$ structure (**8**) (<10% of total Cr) with no such interaction (g $4{\cdot}09_9$, ΔH 42 G; g 1·45, ΔH 41 G) was also observed. Complex (**2**) was reduced to the paired bivalent chromium species (**4**), evolving C_1, C_2, and C_3 hydrocarbons. The u.v. diffuse reflectance spectroscopy revealed that the two adjacent Cr^{2+} ions on Al_2O_3 were not directly σ-bonded. Species (**4**) was converted into the paired monochromate (6+) structure (**7**) with a charge transfer band at 386 nm. The Cr^{6+} ions were reduced again to (**4**) taking H_2 up stoicheiometrically at 870 K.



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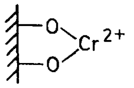

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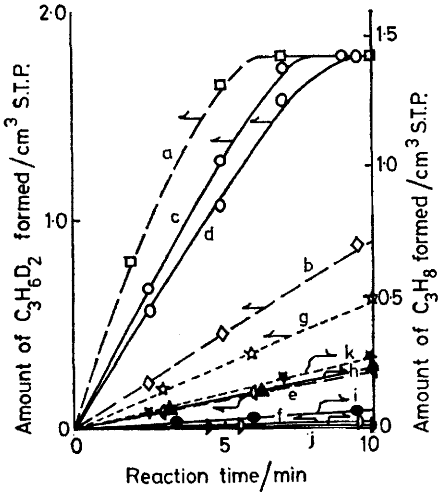

FIGURE. Catalytic activity of the fixed and impregnation catalysts for hydrogenation or deuteriation of C_3H_6; activation energies (kJ mol^{-1}) in parentheses. Deuteriation (0·15 g of catalyst, 238 K): (a) virgin Cr/Al_2O_3 (**9**) (14·6 kJ mol^{-1}), (b) reconstructed Cr/Al_2O_3 (**9**) (19·7), (c) virgin Cr_2/Al_2O_3 (**4**) (17·5), (d) reconstructed Cr_2/Al_2O_3 (**4**) (14·6), (e) Cr–allyl/Al_2O_3 (**8**), (f) Cr_2–allyl/Al_2O_3 (**2**), (g) impregnated $Cr^{2\cdot15+}$/Al_2O_3 (22·6); hydrogenation (0·13 g of catalyst, 262 K), (h) Cr–O–Cr/SiO_2 (**5**) (13·8 kJ mol^{-1}), (i) Cr– –Cr/SiO_2 (**3**) (15·5), (j) Cr_2–allyl/SiO_2 (**1**), (k) impregnated $Cr^{2\cdot05+}$/SiO_2 (46·9).

The t.p.h. analysis of the allyl complex (**1**) showed a sharp desorption peak due to propene at 690 K, indicating that the surface species on SiO_2 were uniformly distributed. The u.v. diffuse reflection peak of (**1**) at 553 nm was assigned to a $\delta\rightarrow\delta$ ($^1A_{2u}\leftarrow{}^1A_{1g}$) transition, whence the $Cr^{2+}\text{–}Cr^{2+}$ bond distance could be estimated to be *ca.* 222 pm (assuming a linear relation between peak energies and bond distances).[4] The dinuclear Cr^{2+} complex (**1**) was oxidized to the dichromate structure (**5**), with 468 and 365 nm bands, *via* the grey Cr^+ catalyst (**3**). The dichromate species was reduced with H_2 at 860 K, consuming 4 mol of H_2 per mol of Cr_2, to the oxygen-bridged dinuclear Cr^{2+} structure (**6**) which showed a characteristic band at 800 nm. Structure (**6**) was oxidized stoicheiometrically with O_2 to the dichromate species (**5**).

A disadvantage of the highly active, fixed 'single' Cr^{2+} catalyst [(**9**), Al_2O_3 support][5], which was prepared using a mononuclear complex, $Cr(\eta^3\text{-}C_3H_5)_4$, was the drastic decrease in catalytic activity for C_3H_6 hydrogenation owing to an unfavourable environmental change during oxidation–reduction cycles [$>Cr^{2+} \rightleftharpoons >Cr^{6+}(=O)_2$]. In contrast, the activity of the paired structure (**4**) was not so affected, as shown in the Figure; the number of vacant co-ordination sites on a Cr^{2+} ion decreased from 1·9 to 0·9, but the activation energy of reaction was also reduced from 17·5 to 14·6 kJ mol^{-1}. Co-operative catalysis involving two adjacent Cr^{2+} sites may occur. The surface structures (**1**), (**2**), (**3**), and (**6**), and a conventional catalyst obtained by an impregnation method showed low activities and the species (**5**) and (**7**) were inactive. Consequently the paired structure (**4**) of co-ordinatively unsaturated Cr^{2+} ions was found to be the most active and stable structure for alkene hydrogenation at low temperatures.

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