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Adsorption and Inter-reaction of Hydrogen and Deuterium on Chromias at Low Temperatures

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Summary Deuterium displaces hydrogen from an irreversible, molecular chemisorption on activated chromia at -196 °C without formation of hydrogen deuteride and with an isotope effect of 50 favouring adsorption of deuterium *vs.* hydrogen.

This communication reports the results of an investigation of the molecular chemisorption of hydrogen and deuterium on activated chromias at low temperatures and of the reactions between the two in the adsorbed state. The very large isotope effects which are observed can be considered to result from involvement of a chemical reaction at -196 °C.

Many of the catalytic properties of chromia appear to result from one or both of the pair sites, Cr^{3+}(cus) and O^{2-}(cus) (cus = co-ordinatively unsaturated surface) which are formed by surface dehydroxylation during activation at higher temperatures.[1] The surface concentrations of Cr^{3+}(cus) on amorphous chromia, as measured by the adsorption of carbon monoxide or of oxygen, irreversible at -78 °C, amount to 0·4 sites nm^{-2} after activation at 300 °C and 1·0 sites nm^{-2} at 400 °C.

The excess of oxygen of an amorphous chromia dried in air finally at 135 °C and designated 85W135[2] was removed by treatment with flowing ultrapure hydrogen at 300 °C for 6 h.[2] The sample was then swept with flowing ultrapure helium (<0·05 p.p.m. oxygen content) at 300—500 °C, the highest temperature (T_{act}) being maintained for 12 h. The resulting chromia is symbolized $Cr_2O_3(T_{act})$. $Cr_2O_3(500)$ is microcrystalline α-Cr_2O_3 but at lower T_{act} the chromia is

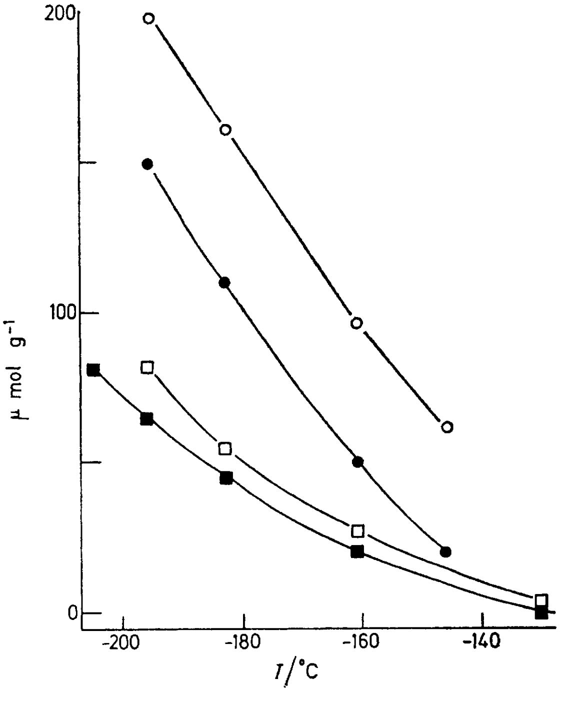

FIGURE. $H_{irr}(T)$ (full symbols) and $D_{irr}(T)$ (open symbols) *vs.* T for $Cr_2O_3(351)$ (squares) and α-$Cr_2O_3(501)$ (circles). Adsorptions are in μmole per g of hydrogen.

amorphous. Pulses of H_2, D_2, HD, CO, O_2, N_2, and Ne were injected into the helium carrier passing over the chromia. Any $H_2 + HD + D_2$ in the flowing helium beyond the chromia was trapped at −196 °C by a Linde 5A molecular sieve which, upon warming, released a pulse for gas chromatographic analysis for H_2, HD, and D_2, or for measurement of quantity by catharometry.

$Cr_2O_3(T_{act})$, usually 0·2 g, was exposed to H_2 at temperature T between −205 and −130 °C for 15 min and then swept with helium at the same temperature for 30 min. Considerable variation in these times produced negligible difference in result. Warming the chromia liberated the irreversibly adsorbed H_2 as a pulse, the amount of which was measured. The adsorption so measured is designated $H_{irr}(T)$. All H_2 was desorbed by −100 °C. As shown in the Figure, $H_{irr}(T)$ decreases steadily with T, becomes zero at *ca.* −130 °C, and $D_{irr}(T)$ always exceeds $H_{irr}(T)$. $H_{irr}(-196)$ increases with T_{act} somewhat more rapidly than $CO_{irr}(-78)$. $H_{irr}(-196)/CO_{irr}(-78)$ is 0·32 at $T_{act} = 300$ °C, 0·43 at 460 °C, and 0·58 at 522 °C. A sample of chromia initially dried at 25 °C and free of excess of oxygen[2] gave essentially the same results when it was activated without initial treatment in hydrogen at 300 °C.

Pulses of D_2 displace H_2 from H_{irr} but pulses of neon at −196 °C do not. $H_{irr}(-196)$ is zero on chromia containing $CO_{irr}(-78)$ or $O_{2\,irr}(-78)$. Thus, H_{irr} is site-selective and displacement does not depend upon the strength of physisorption of the displacing gas. H_{irr} is, therefore, best classified as a weak chemisorption and displacement by D_2 as a chemical reaction. Weak, molecular, site-selective chemisorptions which, however, are reversible at −196 °C are known on activated alumina[3] and zinc oxide.[4]

At −196 °C, pulses of D_2 (0·104 cm^3) were passed over $Cr_2O_3(350)$ containing $H_{irr}(-196)$. The exit pulses from the first two injections contained 100% H_2, the third 82% H_2 + 18% D_2, and the fourth 100% D_2. Warming liberated 100% D_2. At −161 °C, the first pulse contained 100% H_2, the second 32% H_2 + 20% HD + 48% D_2, the third 3% HD + 97% D_2, and the fourth 100% D_2. HD completely displaces H_2 from H_{irr} at −196 °C and D_2 displaces HD from HD_{irr}. Displacement of H_{irr} by D_2 at −196 °C without formation of HD is also observed on $Cr_2O_3(525)$ and Cr_2O_3–SiO_2 (made by reduction in H_2 at 294 °C of Davison Grade 62 silica gel containing 4·58 wt. % of CrO_3). Pulses of H_2 displace D_2 from $D_{irr}(-196)$ but much less sharply than in the reverse reaction. No HD is formed at −196 °C, but at −161 °C more HD is formed than in the reverse reaction.

To characterize further the large isotope effect evident in this work, a mixture of mole ratio $H_2/D_2 = 19$ was passed over $Cr_2O_3(375)$ at −196 °C to a steady state, the chromia was swept with helium, and the $(H,D)_{irr}$ released by warming was analysed. Under these conditions, our sensitivity, 1—2%, permitted measurement of the H_2 content both of the gas and of the adsorbate. $[D_{irr}/H_{irr}]/[D_2(g)/H_2(g)]$ was *ca.* 50.

At −196 °C, H_{irr} probably involves molecular, polarization adsorption at Cr^{3+}(cus) O^{2-}(cus).[3–5] Since some interaction of D_2 with $*H_2$ appears to be necessary in the displacement, the displacement can be represented by the sequence (1),

$$*H_2 + D_2(g) \rightarrow D_2*H_2 \rightarrow D_2* + H_2(g) \qquad (1)$$

and the isotope effect appears in the last step. At somewhat higher temperatures, D_2*H_2 must rearrange to $(HD)*(HD)$ perhaps *via* $H^-*(HD_2)^+$. We cannot however, exclude displacement by $H_2* \rightarrow H_2'(g)^+*$ followed by $D_2(g)^+* = D_2*$, where $H_2(g)$ is in equilibrium with H_2* and $P(H_2)$ (equil.) falls rapidly with coverage,

The surface hydroxyl ions of chromia, O_SH^-, do not change detectably with pulses of D_2 below 0 °C. Since both heterolytic and reductive dissociative adsorption[1] would generate O_SD^- amidst O_SH^-, these dissociative forms of adsorption are unlikely to be involved in the experiments at lower temperatures.

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