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Hydrogenation of Olefins and Polymerization of Ethene over Chromium Oxide/Silica Catalysts

II. Interaction with Hydrogen

P. P. M. M. WITTGEN,[1] C. GROENEVELD,[2] J. H. G. J. JANSSENS,
M. L. J. A. WETZELS, AND G. C. A. SCHUIT

Department of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, The Netherlands

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The hydrogen uptake of chromium oxide/silica catalyst shows a partial similarity with that of α-Cr_2O_3 as reported by Weller and Voltz [*J. Amer. Chem. Soc.* 76, 4695 (1954)]. At low temperatures a heterolytic dissociative adsorption of H_2 occurs at a site consisting of two Cr^{3+} ions and two oxygen anions. At high temperatures a subsequent reaction occurs leading to reduction of Cr^{3+} to Cr^{2+} followed by a dissociation of water. The Cr_2O/silica catalyst differs from the α-Cr_2O_3 sample of Weller and Voltz because water is not expelled but reacts with silica under formation of silanol groups. At still higher temperatures this reaction is reversed by an interaction of the silanol groups with Cr^{2+} producing Cr^{3+} and H_2.

INTRODUCTION

A study of the adsorption of H_2 and olefins is a necessary prelude to unravelling the reaction mechanism of olefin hydrogenation over CrO_x/SiO_2 catalysts. The present paper is concerned with the adsorption of H_2. Adsorption of olefins in the absence of hydrogen can lead to polymerization and will be discussed separately in a later paper.

The adsorption of hydrogen on pure chromia is extensively described in the literature, for instance by MacIver and Tobin (*1*) but in particular by Weller and Voltz (*2*). Weller and Voltz found two different types of H_2 adsorption, one at low temperature ($T < 100°C$) and another at high temperature ($T > 200°C$). They ascribed the adsorption at high temperature to reduction of the chromic ions to chromous ions. In view of the occurrence of H_2/D_2 exchange at low temperatures, the low temperature adsorption must be of chemical nature.

In this paper we report on a study of the H_2 uptake of chromia dispersed on silica, performed in order to ascertain whether it is analogous to the processes observed by the researchers mentioned above. For the sake of convenience, the interaction with hydrogen will be denoted further as adsorption.

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[1] Present address: Chemical Laboratory, TNO, Lange Kleiweg 137, P.O. Box 45, Rijswijk (ZH), The Netherlands. To whom correspondence should be addressed.

[2] Present address: Central Research Laboratory, Dutch States Mines, P.O. Box 18, Geleen, The Netherlands.

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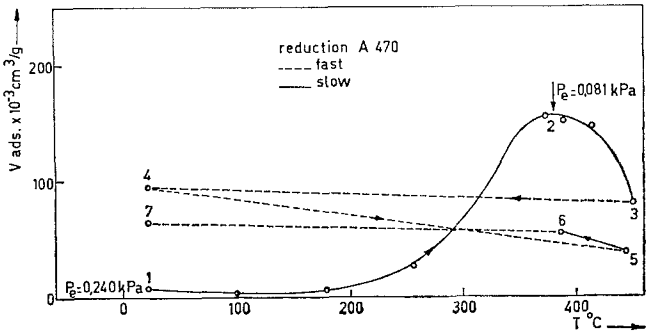


FIG. 1. Hydrogen adsorption runs at constant hydrogen amounts on 2 wt% Cr catalyst (II A reduced at 470°C) (P_e = equilibrium pressure).

EXPERIMENTAL

Catalyst. The 2.0 wt% Cr catalysts were prepared by impregnation of silica gel (Davison grade 12; 600 m^2/g) with chromic acid solution according to the impregnation method II described in Part I (*3*). The catalysts were dried, calcined at 500°C for 4 hr and stored in a dry atmosphere.

Apparatus and pretreatment of the catalyst. The principle of the hydrogen adsorption measurements was to measure the pressure change as result of the hydrogen taken up by the catalyst. The measurements were carried out in a conventional adsorption apparatus. Prior to the measurements the samples could be reduced at 470–600°C with hydrogen in the adsorption apparatus itself either in a static hydrogen atmosphere (method A or A′, pressure 90 or 0.8 kPa, respectively), or in a stream of hydrogen (method B or B′: hydrogen flow over the catalyst or through the catalyst bed, respectively; space velocity 100 cm^3/min, pressure 0.1 MPa); in the case of methods A and A′ the sample was previously reduced in a separate dynamic system and subsequently exposed to air.

Catalysts after reduction A, A′, and B were green. Catalysts after reduction B′ were blue, presumably because of effective removal of the water evolved (*3*). Evacuation (<1.3 mPa; T = 500°C) before the adsorption measurements changed the color again into green unless the reduction (B′) was carried out for a longer time.

All catalysts were green after reduction unless otherwise stated.

RESULTS

Adsorption at Constant Amounts of Hydrogen

Hydrogen adsorption was measured for catalysts (II A), (II B) and (II B′). All runs show two different adsorptions when measured from low to high temperature (Figs. 1 and 2 points 1 → 2 → 3 etc.), viz., one at low temperature (T < 100°C; abbreviated L.T.) and an activated one at high temperature (T > 200°C; abbreviated H.T.). The L.T. adsorption is fast and reversible but small compared with the H.T. adsorption. In contrast with the activated adsorption at high temperature measured after reduction method B, the activated H.T. adsorption after reduction method A is irreversible. Decreasing the temperature (Fig. 1: 3 → 4) and after that increasing the temperature (4 → 5) in run A does not reproduce adsorption point 3. On slowly decreasing the temperature (5 → 6) an adsorption maximum is obtained that is difficult to reproduce. After reaching the adsorption maximum in isobar Bb this isobar is completely reversible. The explanation for this different behavior is most probably a continuing reduction in the case of catalyst

(II A). Apparently the reduction of the catalyst by reduction method A is not complete. The water evolved during the reductive adsorption diffuses to colder sections of the apparatus and partially compensates the hydrogen uptake.

Also the adsorption of hydrogen on pure silica appears to be different after the pretreatment A or B. In the case of method A the adsorption decreased with increasing temperature but was negligible compared to the adsorption on a reduced catalyst. In the case of method B the adsorption on silica was at first nil up to 300°C but after adsorption at high temperature ($T > 300°C$) a hydrogen uptake could be measured also at low temperature.

Isotherms

L.T. H_2 isotherms are represented in Fig. 3, tabulated in Table 1, and compared with the different adsorption models (*4*), viz., models with the heat of adsorption either independent of coverage (Langmuir models) or dependent on coverage (Freundlich and Temkin models).

Figure 3 shows that with a higher degree of reduction of the catalyst less hydrogen adsorption takes place at low temperature. This is reflected by the isotherms 1 and 2 of catalysts reduced in the static system with a hydrogen pressure of 0.8 kPa (method A′) which show a higher adsorption than isotherm 4 measured on a catalyst reduced at 90 kPa (method A). In the latter case an even smaller adsorption is observed after initial adsorption of hydrogen at 400°C (isotherm 5). Presumably because of the fact that the reduction of the catalyst according to method B is even more complete, the adsorption at 20°C is not measurable. For

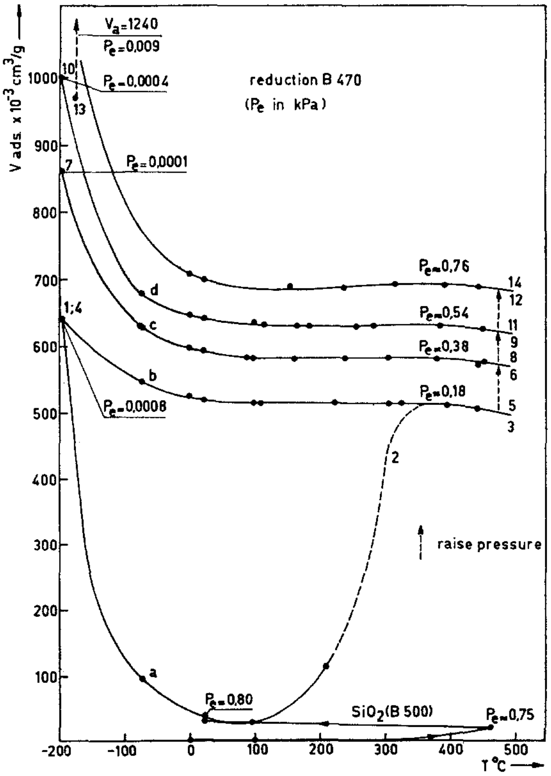


FIG. 2. Hydrogen adsorption runs on 2 wt% Cr catalyst (II B reduced at 470°C) and pure silica gel (II B reduced at 500°C).

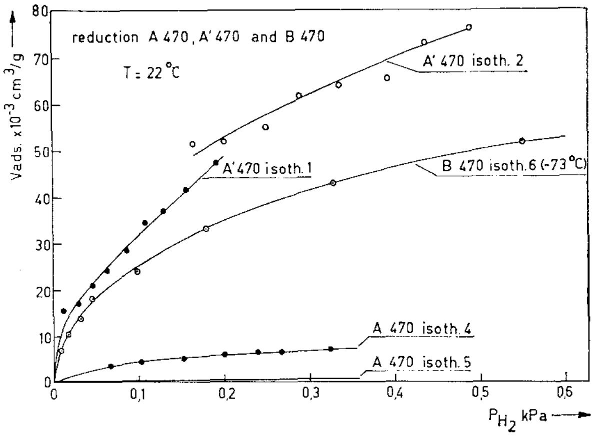


FIG. 3. Hydrogen adsorption isotherms on 2 wt% Cr catalyst (A, A′, and B reduced at 470°C).

that reason the adsorption (isotherm 6) was measured at −73°C.

When the L.T. isotherms are compared with the different adsorption models the Freundlich model gives the best fit. Because of poor reproducibility for different

TABLE 1

Low Temperature and High Temperature Isotherms[a]

Number	Isotherm	Langmuir						Freundlich		Temkin
		Associative			Dissociative					
		$\theta=\frac{V}{V_m}=\frac{p}{p+p^0}$			$\theta=\frac{V}{V_m}=\frac{p^{\frac{1}{2}}}{p^{\frac{1}{2}}+p^{0\frac{1}{2}}}$			$V=cp^{1/n}n>1$		$V=\frac{1}{a}\ln c_0p$
		V_m (cm³/g)	p^0 (Pa)	r	V_m (cm³/g)	p^0 (Pa)	r	$1/n$	r	r
1	22°C adsorption A′ 470	0.038	23	0.872	0.107	592	0.944	0.45	0.970	0.934
2	22°C adsorption A′ 470	0.098	167	0.952	0.245	2600	0.970	0.39	0.977	0.970
—										
4	22°C adsorption A 470	0.009	93	0.977	0.026	2370	0.989	0.40	0.986	0.977
—										
6	−73°C desorption B 470	0.037	43	0.983	<0	—	0.998	0.49	0.997	0.978
7	400°C adsorption[b] B 470	0.736	85	0.965	0.990	172	0.984	0.21	0.993	0.985
8	450°C adsorption[b] B 470	0.739	95	0.966	1.02	209	0.985	0.22	0.993	0.985
9	460°C adsorption B 470	0.620	5	0.995	0.727	5.9	0.999	0.14	0.989	0.994
10	550°C desorption B 600	0.649	10.4	0.945	0.728	6.7	0.986	0.10	0.995	0.995
11	460°C desorption B 500	0.368	17.3	0.978	0.550	59.6	0.986	0.24	0.979	0.984
12	460°C desorption[c] B 500	0.327	45	0.985	0.629	377	0.977	0.31	0.975	0.998
13	400°C desorption[c] B 500	0.252	4.4	0.958	0.274	2.3	0.995	0.075	1.00	1.00
14	460°C desorption B′ 500	0.408	30	0.988	0.559	73.2	1.00	0.21	1.00	1.00

[a] θ, degree of coverage; V, volume of adsorbed gas; V_m, volume of monolayer; r, correlation coefficient; p, pressure; p^0, pressure at $\theta = 0.5$; c, c_0, a, n, constants.

[b] Isotherms determined from adsorption "isobars" (Fig. 2).

[c] Isotherms measured with the same sample.

samples a further characterization of the adsorption is difficult, but of the two Langmuir models the dual site model gives a better fit. That the dual site model fits best is easily understood because the Freundlich approximation results in $1/n \approx \frac{1}{2}$ and a dual site adsorption at low pressure ($p \ll p^0$) can be approximated by

$$V = \frac{V_m}{(p^0)^{\frac{1}{2}}} \cdot p^{\frac{1}{2}} \qquad (1)$$

where V_m = volume of monolayer and p^0 = pressure at $V = \frac{1}{2}\, V_m$. In Table 1 also the H.T. adsorption isotherms are represented. The H.T. isotherms measured on the different catalyst samples are badly reproducible. When the H.T. isotherms are compared with the different adsorption models the Freundlich and Temkin models give the best fit. Of the two Langmuir models the dual site model gives a better fit, which corresponds with the literature (*2*).

Starting from the assumption that a dual site model is a good description for both adsorptions, the variations in V_m and p^0 of the H.T. as well as the L.T. isotherms point to a large influence of surface conditions on the hydrogen adsorption.

DISCUSSION

The results of the adsorption measurements will be evaluated on the basis of the hydrogen adsorption measurements on pure α-Cr_2O_3 reported by Weller and Voltz (*2*). The surface area of their samples was about 35 m^2/g which corresponds to 570 μmol chromium at the surface, assuming a cubic close-packed lattice of oxygen ions (surface area 0.068 nm^2) in which two of the three octahedral cation positions are occupied by chromium ions. With atomic dispersion of chromium in CrO_x/SiO_2 (2 wt% Cr) the number of chromium ions at the surface amounts to 380 μmol, hence reasonably similar to the Weller and Voltz situation.

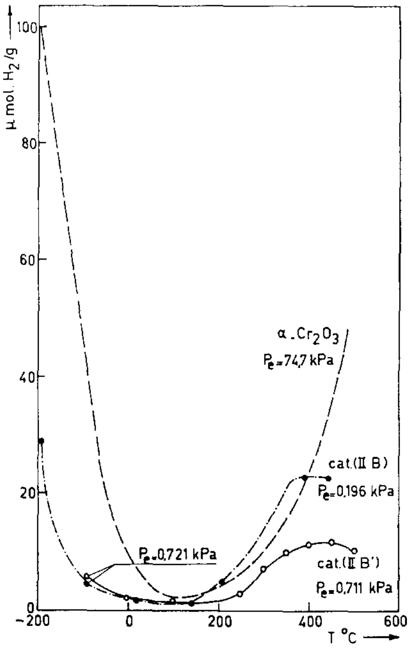


FIG. 4. Comparison of the hydrogen adsorption runs on α-Cr_2O_3 measured by Weller and Voltz (*2*) and the adsorption runs (II B 470) and (II B′ 500).

Figure 4 shows the run of Weller and Voltz, the run on the green catalyst (II B), and the run on the blue catalyst (II B′). There are differences as well as similarities between the runs presented here and that of Weller and Voltz. One of the similarities is the presence of two temperature regions in which adsorption takes place: one at low temperature and one at high temperature. The H.T. adsorption is in both cases an activated one. Also the amounts adsorbed are comparable. The differences are given by the absence of an adsorption maximum at high temperature and a much larger adsorption at very low temperatures in the Weller and Voltz run.

L.T. Adsorption

The differences in the amount of hydrogen adsorbed on pure chromia and on catalysts (II B) and (II B′) can be ascribed mainly to the hydrogen pressure used during the adsorption. Weller and Voltz

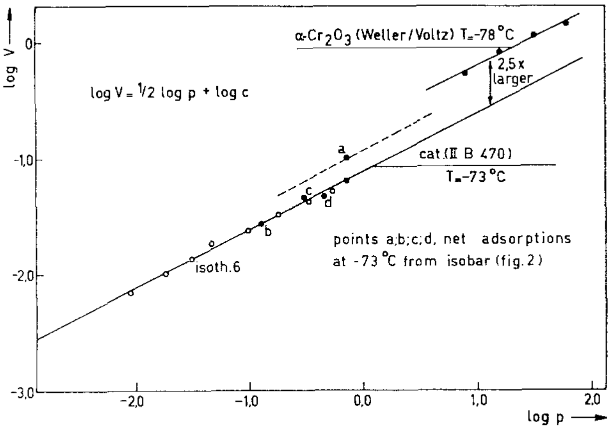


FIG. 5. Freundlich isotherms: isotherm 6 (−73°C) and isotherm (−78°C) measured by Weller and Voltz (*2*). Points (a), (b), (c), and (d) have been taken from run (II B 470).

used 74.7 kPa, whereas we used 0.67 kPa.

The Freundlich model and to a lesser extent the Langmuir dual site model are reasonably good descriptions of the L.T. adsorption. In fact at low coverage ($p \ll p^0$) the Langmuir dual site model can also be described by the Freundlich approximation with $n = 2$:

$$V = cp^{\frac{1}{2}} \qquad (2)$$

where c is a constant. For example, plotting isotherms 6 according to:

$$\log V = \tfrac{1}{2} \log p + \log c \qquad (3)$$

results in a straight line (Fig. 5). The comparable isotherm of Weller and Voltz measured at −78°C (*2*) is also plotted in the figure. It is noteworthy that both isotherms are parallel to each other, the amount adsorbed in the Weller and Voltz isotherm being 2.5 times larger. This combined with the fact found by Weller and Voltz that the amount adsorbed at −196°C is about 130 μmol H_2 results in 52 μmol H_2 at −196°C for the CrO_x/SiO_2 system. So in the case of Weller and Voltz as well as in our case there exists a fast but weak dissociative adsorption which is not covering the total amount of surface chromium (coverage of surface chromium, 23 vs 14%).

In both systems the L.T. adsorption appears to be influenced by the degree of reduction and the presence on the surface of hydrogen previously adsorbed at high temperature (e.g., compare isotherm 4 and 5). This is also confirmed by plotting the adsorption values at −73°C from isobar B in Fig. 5. Point (a) is the amount of adsorbed hydrogen on a clean evacuated catalyst surface, points (b), (c), and (d) represent the amounts of adsorbed hydrogen on a hydrogen-covered surface. The straight line according to the Freundlich equation with $n = 2$ drawn through point (a) is situated at higher volumes than the parallel line through (b), (c), and (d).

H.T. Adsorption

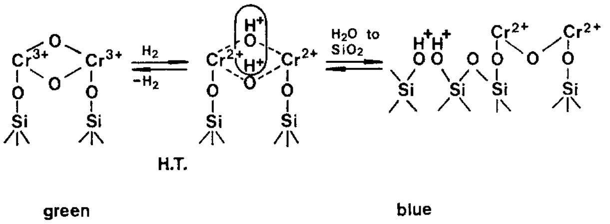
Catalysts (II B) and (II B′) show a maximum in the activated H.T. adsorption. Weller and Voltz presume that there will be a maximum at higher temperatures as a result of sintering; however, they did not find evidence for it. The adsorption maxima of catalysts (II B) and (II B′) cannot be ascribed to sintering effects because of the reversible character of the process. Besides the possibility of sintering Weller and Voltz found evidence for the reduction of the chromium oxide:

$$Cr_2O_3 + H_2 \rightleftharpoons 2CrO + H_2O \qquad (4)$$

viz., (i) in a static system the hydrogen adsorption is much smaller than in a circulation apparatus with cold trap equipment, and (ii) a hydrogen evolution by adding water to the hydrogen-treated oxide at high temperature as confirmed by other investigators (*5*, *6*). Evidence for reductive adsorption in our experiments has been found in isobar A. At temperatures above the adsorption maximum no reversible adsorption–desorption process is present. This must be ascribed to the evolution of water. In isobar B the adsorption maximum is reproducible. The fact that Weller and Voltz did not detect this adsorption maximum can be explained only when the adsorption process is described as follows:

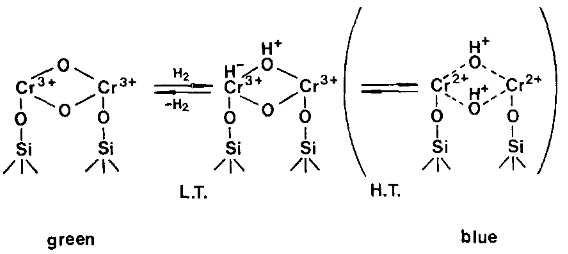
$$\begin{array}{lrl}
\alpha - Cr_2O_3: & Cr_2O_3 + H_2 \rightleftharpoons Cr_2O(OH)_2 & \left.\begin{array}{l} \\ \\ \end{array}\right| \text{endothermic} \qquad (5) \\
\text{(Weller and Voltz)} & Cr_2O(OH)_2 \rightleftharpoons 2CrO + H_2O & \qquad\qquad\qquad\qquad (6) \\
CrO_x/SiO_2: & Cr_2O_3 + H_2 \rightleftharpoons Cr_2O(OH)_2 & \left.\begin{array}{l} \\ \\ \end{array}\right| \text{exothermic} \qquad (7) \\
 & Cr_2O(OH)_2 + SiO_2 \rightleftharpoons 2CrO + SiO(OH)_2 & \qquad\qquad\qquad\qquad (8) \\
 & SiO(OH)_2 \rightleftharpoons SiO_2 \cdot H_2O & \qquad\qquad\qquad\qquad (9)
\end{array}$$

The amount of adsorbed hydrogen will increase with increasing temperature because of the endothermic character of the reduction [Eqs. (5, 6)]. This process will be promoted by the presence of a cold trap by which the water evolved will be removed. With the CrO_x/SiO_2 catalyst this process will be influenced by adsorption of water at the silica surface. In first instance the H_2 adsorption increases with increasing temperature because it is an activated process, but because of the exothermic character of the process [Eqs. (7, 8)] the reaction will be reversed above 400°C. Since H_2O adsorption on silica is undoubtedly connected with the formation of silanol groups on the silica surface (*7*, *8*) the H.T. adsorption and its reversal can now be summarized by the following model:



(10)

With this picture of the H.T. adsorption it is evident why a further reduced catalyst adsorbs less hydrogen at high temperature. It is also evident why the color of the further reduced catalyst does not turn into green on evacuation. The evacuation tends to dissociate water from the silica support which then reoxidizes Cr^{2+} to Cr^{3+}. Long times for reduction serve to rereduce the Cr^{3+} thereby removing water from the catalyst. The negative influence on the L.T. adsorption of an excessive reduction or of the adsorption of hydrogen at high temperature points to chromium(III) instead of chromium(II) as the adsorption site for the L.T. dual site adsorption:



(11)

Evidence for this kind of heterolytic adsorption at room temperature is presented by Eischens *et al.* (*9*) and Kokes (*10*) for the adsorption of hydrogen on zinc oxide. A heterolytic low temperature adsorption was earlier proposed by Stone and Vickerman (*11*) for Cr^{3+}-solid solution in α-Al_2O_3.

In Part I (*3*) the elements of the model given above were assembled and its consequences have now been illustrated in more detail. It is shown here that the situation of the catalyst is not only dependent on the method of reduction but also on what follows thereafter because of the intrinsic ability of a reaction between Si–OH and Cr^{2+}. The "H_2 uptake" cannot therefore be treated as a simple adsorption or chemisorption on one component Cr^{n+}; it is connected with an interaction of this component with the carrier. In later papers we will show that this is essential for the understanding of the hydrogenation–dehydrogenation and polymerization properties of the catalyst.

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