

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

## III. Hydrogenation of Olefins and H/D Exchange

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The hydrogenation of olefins over  $\text{CrO}_x/\text{SiO}_2$  catalysts was investigated by pulse experiments, circulating gas studies, and steady-state continuous flow experiments. Around room temperature the reaction is of first order in  $\text{H}_2$  while the order for the olefin concentration is between zero and one. The activation energy is very low ( $\sim 10 \text{ kJ mol}^{-1}$ ) and small amounts of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , etc., inhibit the reaction entirely. At temperatures between 150 and  $300^\circ\text{C}$  the catalyst decays in  $\text{H}_2$  (activation energy  $\sim 40 \text{ kJ mol}^{-1}$ ). Above  $350^\circ\text{C}$ , however, the catalyst becomes active again: HTR-kinetics are first order in olefin and around zero order in  $\text{H}_2$ . A model was set up based on the mechanism proposed by Burwell with the active sites being binary  $\text{Cr}^{3+}$  complexes. The active complex is anchored on the silica surface, and is probably identifiable by its ESR signal ( $\delta$ -signal). The deactivation is due to a reduction. This is an exothermic process presumably because the  $\text{H}_2\text{O}$  formed remains adsorbed on the silica surface. Because of its exothermicity the reducing adsorption becomes reversed at higher temperatures and the catalyst is reactivated (heat of adsorption  $63 \text{ kJ/mol H}_2$ ).

### INTRODUCTION

The present paper is the third in a series aimed at the elucidation of the catalytic properties of  $\text{CrO}_x/\text{SiO}_2$  for reactions such as the hydrogenation and polymerization of olefins. The first paper by Groeneveld *et al.* (1) was concerned with the preparation of the catalyst and its structure. The second (Wittgen *et al.* (2)) reported on experiments to study the interaction of the catalyst with  $\text{H}_2$ .

The investigation presently described was primarily concerned with the catalytic hydrogenation of olefins while some attention was given to the  $\text{H}_2/\text{D}_2$  equilibration and to the ways in which the two reactions influenced each other. Experiments were performed via the pulse method to explore the field. These were subsequently completed by continuous flow (steady-state) experiments in which the kinetics of the reactions were measured more quantitatively. Experiments on the  $\text{H}_2/\text{D}_2$  equilibrations were performed in an apparatus with the gases circulating over the catalyst. The investigations were terminated in 1974 and the results reported in the thesis of the principal author (Wittgen, 3); since a complete description of apparatus and analytical methods was given there, these will be mentioned here only briefly.

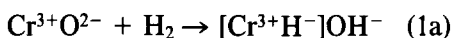
Chromium catalysts have been the subject of various investigations. Extensive

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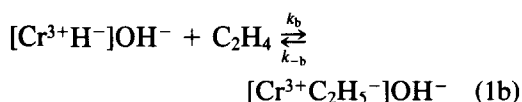
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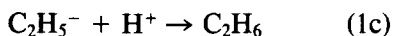
studies by Burwell (4–8) and Selwood (9–11) have produced a considerable amount of information on the olefin hydrogenation and H<sub>2</sub>/D<sub>2</sub> equilibration over pure Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. From this work Burwell proposed a model for the mechanism of the reaction. The site was supposed to consist of a Cr<sup>3+</sup> cation and an oxygen anion, the Cr<sup>3+</sup> cation being accessible from the gas phase because it was situated next to a surface anion vacancy (cus). Hydrogen was assumed to become adsorbed by heterolytical fission with the hydride ion becoming connected to the cation in the cus and the proton being bonded by the oxygen:



The olefin subsequently formed a carbanion by reaction with the hydride ion:



The final reaction was the combination of carbanion and proton to form the paraffin:



When D<sub>2</sub> was used instead of H<sub>2</sub> the results depended on the temperature indicating that there might be more than one type of reaction. At temperatures below 100°C the D<sub>2</sub> molecule became attached to the double bond without any randomization of the hydrogen and deuterium atoms from olefins and D<sub>2</sub>. At higher temperatures, however (>300°C), H/D exchange became rather extensive. In Burwell's model it was assumed that this is caused by the ratio  $k_{-b}/k_b$  being low at the lower temperature while at higher temperatures  $k_{-b} \gg k_b$ .

While Burwell proposed that the active cation is Cr<sup>3+</sup>, van Reyen *et al.* (12) argued that it might be Cr<sup>2+</sup>. However, their catalytic activity was determined with reference to the dehydrogenation of cyclohexane to benzene instead of the hydrogenation of olefins; the two reactions are not necessarily similar in their mecha-

nisms. They also studied the CrO<sub>x</sub>/SiO<sub>2</sub> catalyst that was found to be similar in properties.

Selwood (9–11), Schaefer *et al.* (13, 14), and Stone and Vickermann (15) studied the H<sub>2</sub>/D<sub>2</sub> equilibration on the surfaces of solid solutions of Cr<sub>2</sub>O<sub>3</sub> in α-Al<sub>2</sub>O<sub>3</sub>, while Schaefer also investigated the hydrogenation of ethene at 20°C over this catalyst. He mentioned that activation in a He stream after reduction by H<sub>2</sub> produced superior catalysts for both the hydrogenation and the H<sub>2</sub>/D<sub>2</sub> equilibration provided the reaction temperature remained between –100 and 200°C. At higher temperatures the He-activated catalyst decayed in activity to a level that was similar to that of the H<sub>2</sub>-activated samples. Selwood reported that a hydrogen treatment at 500°C completely deactivated the catalyst that can, however, be reactivated by passing O<sub>2</sub> over it followed by reduction in H<sub>2</sub> above 275°C. The activity of the catalyst increases with the temperature of reduction but this was accompanied by an increasing instability as manifested by a faster decay. Selwood concluded from these observations that the active cation was trivalent chromium. Stone and Vickermann activated their catalysts by a treatment in air at 1250°C followed by an evacuation at 850°C. They observed that the rate of H<sub>2</sub>/D<sub>2</sub> equilibration increased from –100°C upward to about 0°C to decrease subsequently after a further rise in the temperature. By 200°C the rate as compared with that at 0°C had fallen by a factor of 10. At still higher temperatures it increased again. A pretreatment of the catalyst with H<sub>2</sub> led to a much lower activity at –23°C. A most interesting observation was that the rate increased with the second power of the Cr concentration leading to the supposition that the catalytic site contains two Cr<sup>3+</sup> cations. This might be rationalized by assuming that the reduction:



is a concerted process. There would then

be no need to introduce a rapid migration of hydrogen atoms along the surface (16) to explain the reduction to single metal sites. The model of Stone and Vickermann for the structure of the active site is that of a pair of octahedrally surrounded  $\text{Cr}^{3+}$  cations with the octahedra sharing a face.

Denisova *et al.* (17) studied the olefin hydrogenation over  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  as a function of the temperature. The rate increased with the temperature but at temperatures higher than  $150^\circ\text{C}$  a decay set in that was fast at  $250^\circ\text{C}$ . At higher temperatures the decay became less pronounced and the overall conversion increased again. When, starting from  $400^\circ\text{C}$ , the temperature was lowered, the rate steadily decreased, and the original low-temperature reaction could not be observed any more. The reaction at high temperatures was found to be of first order in propene and of zero order in hydrogen; the activation energy was  $40 \text{ kJ mol}^{-1}$ . More recently Indovina *et al.* (18) studied the  $\text{H}_2/\text{D}_2$  equilibration over  $\text{CrO}_x/\text{SiO}_2$  catalysts that were reduced at  $350^\circ\text{C}$  by CO after an extensive pretreatment by  $\text{O}_2$  followed by evacuation up to  $700^\circ\text{C}$ . The catalyst was believed to contain almost exclusively  $\text{Cr}^{2+}$ . It was active for the  $\text{H}_2/\text{D}_2$  equilibration, the rate being linearly related to the amount of chromium. No decay in activity was observed. The activity is smaller than for  $\text{Cr}^{3+}/\text{SiO}_2$  but readily measurable; the activation energy was quite low ( $5 \text{ kJ mol}^{-1}$ ).

The results of the various investigations show common features although there remain discrepancies. One very common observation is that active catalysts can only be obtained after some pretreatment, an evacuation, or a passage of an inert gas over the catalyst at temperatures as high as  $750^\circ\text{C}$ . This is presumably connected with the necessity to create surface anion vacancies. A similar treatment in  $\text{H}_2$ , however, destroys the catalytic activity at temperatures around  $300^\circ\text{C}$ . This might be caused by the reduction of  $\text{Cr}^{3+}$  to  $\text{Cr}^{2+}$ . There is, however, no unanimity on the problem

whether  $\text{Cr}^{2+}$  catalysts can catalyze the hydrogenation of olefins.

#### EXPERIMENTAL

*Catalyst preparation.* The  $\text{CrO}_x/\text{SiO}_2$  catalysts (usually 2 wt% Cr) were prepared by impregnation of Aerosil-Degussa (surface area  $200 \text{ m}^2/\text{g}$ ) or more frequently Davison silica gel grade 12 (surface area  $600 \text{ m}^2/\text{g}$ , pore volume 0.4). The mesh size of the silica gel as received was 28–200; mesh size fractions usually applied were 28–80 mesh. Two methods of impregnation, both with a chromic acid solution (1) were applied. Method I ("incipient wetness") consisted of an impregnation with a small volume of a relatively concentrated solution; the support absorbed all of the solution. In method II ("ion exchange") the support was suspended in a relatively large but dilute solution of the chromic acid; after a few hours of immersion under stirring the solid was filtered. All samples were dried for 16 hr at  $105^\circ\text{C}$ , separated into two fractions viz.,  $0.9 < \phi_p < 0.175 \text{ mm}$  and  $0.175 < \phi_p < 0.600 \text{ mm}$  ( $\phi_p$  = particle diameter), calcined in air for 4 h at  $500^\circ\text{C}$  and stored over  $\text{P}_2\text{O}_5$ . The standard method of reduction was heating in a current of  $\text{H}_2$  ( $40 \text{ cm}^3/\text{min}$ ) with increasing temperature ( $15^\circ\text{C}/\text{min}$ ) ending with 1–4 hr at  $475\text{--}500^\circ\text{C}$ . Catalysts so prepared were green (I green and II green). Some samples of catalyst II were reduced at a higher hydrogen flow rate ( $>100 \text{ cm}^3/\text{min}$ ) and a slower rate of temperature increase ( $10^\circ\text{C}/\text{hr}$ ). These catalysts were pale blue (II blue).

*Gases and their purification.*  $\text{H}_2$  was obtained from LOOSCO cylinder, was first passed over BTS catalyst (Cu on support, BASF) and subsequently over Ni-on-aerosil ( $400^\circ\text{C}$ ) to remove  $\text{O}_2$  and CO, followed by a passage through an empty cold trap (cooled by liquid  $\text{N}_2$ ) and another cold trap (liquid  $\text{N}_2$ ) with type A Union Carbide molecular sieve. In later experiments the BTS and Ni-aerosil were replaced by a Pd-diffusion cell operating at 10–20 atm and  $200\text{--}300^\circ\text{C}$ . Results obtained by using  $\text{H}_2$

purified according to these two methods did not show significant differences.

He and Ar were passed over the BTS catalyst to remove O<sub>2</sub> and via a molecular sieve cold trap, cooled to -196°C for He and -70°C (acetone-solid CO<sub>2</sub>) for Ar.

CO and hydrocarbons first passed a BTS catalyst to remove O<sub>2</sub> and subsequently a molecular sieve trap maintained at 20°C.

O<sub>2</sub> and air were only purified by passing them over a molecular sieve trap maintained at 20°C.

*Apparatus: Hydrogenation of olefins (for details see Wittgen (3)).* (a) Pulse method: pulses of olefins (2–6 cm<sup>3</sup>) were injected into a hydrogen stream (usually 40 cm<sup>3</sup>/min) passing through a glass reactor ( $\phi_i = 9$  mm) filled with catalyst (wt 0.1–0.75 g). The total pressure at the reactor inlet was ~1.4 atm absolute. (b) Continuous flow (steady state) method: Mixtures of H<sub>2</sub>, olefin, and He flowed through the glass reactor filled with catalyst (0.10–2.50 g). The velocity of the gas stream was 20–40 cm<sup>3</sup>/min at 1 atm absolute.

*Apparatus for hydrogen/deuterium equilibration and exchange (3).* The experiments were performed in a glass circulation apparatus. Its total volume was 375 cm<sup>3</sup> including a mixing vessel (225 cm<sup>3</sup>), connecting lines, pump (110 cm<sup>3</sup>), and quartz reactor (40 cm<sup>3</sup>). The pump was a Teflon membrane pump (C. Neuberger NKEI, speed 0.3–2 dm<sup>3</sup>/min). The tubing was for the greater part made from glass with some flexible metal connections. Lubrication for cocks and connection was performed with apiezon M. At regular times gas samples were stored in loops; their contents were analyzed after the run was terminated. The reactor contained a central thermowell with the thermocouple situated at the mid-position of the catalyst.

*Analytical.* Analyses were performed on a gas chromatograph with thermal conductivity cell. Hydrocarbons were separated on a 3 mm column 10 m long of chromosorb. For H<sub>2</sub>/D<sub>2</sub>/HD separations a column was used of ferrihydroxide on alumina with

4 mm diameter and 8 m length at a temperature of -196°C (19). Mass spectroscopic analyses were performed with the AEI-MS10 instrument. The results are further given as  $\eta$  (% conversion of olefin to paraffin) and  $K$ ,

$$K = \frac{[\text{HD}]^2}{[\text{D}_2][\text{H}_2]}$$

## RESULTS

### A. Pulse Experiments

1. *Behavior of the catalyst as a function of run time  $t$  and temperature.* A catalyst was brought into the reactor, precalcined, and reduced by H<sub>2</sub> after which the catalyst was cooled in He to 100°C. At time  $t = 0$  the He stream was replaced by H<sub>2</sub> and pulses of propene were injected at various times  $t$  into the H<sub>2</sub> stream. The conversion of the pulse  $\eta_t$  was determined. Figure 1 shows that  $\eta_t$  decreased with increasing time  $t$ ; plotting  $\log \eta_t$  versus  $t$  gives a straight line:

$$\log \eta_t = \log \eta_0 - \alpha t \quad (3)$$

with  $\eta_0$  the conversion of a pulse introduced at  $t = 0$  and  $\alpha$  a constant (at constant temperature). The following observations were made on the dependency of  $\alpha$  on the number of propene pulses introduced during a certain time interval  $\Delta t$  and of changing H<sub>2</sub> for He for some time. Increasing the number of pulses did not change  $\alpha$  and the catalyst was just as active before as after the He period, that is, the decay was caused by hydrogen or an impurity in hydrogen.  $\alpha$  was strongly dependent on the temperature: if the temperature during the time interval  $\Delta t$  was increased, the decay was more pronounced. Catalysts II blue and I differ somewhat in properties: the former is more active (greater  $\eta_0$ ) but also less stable (greater  $\alpha$ ). Attempts to decrease  $\alpha$  by changing the purification of the H<sub>2</sub> failed entirely; neither increasing the number of guard reactors nor choosing other purification methods gave any improvement. We therefore conclude that the

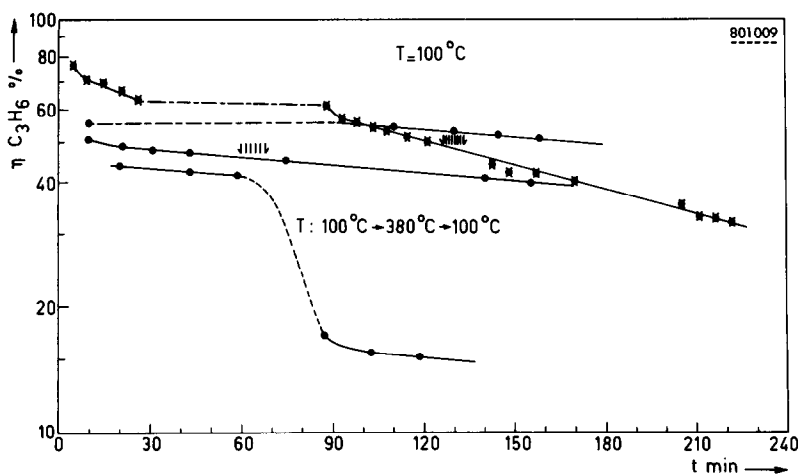


FIG. 1. Hydrogenation of propene pulsed in  $H_2$ . Conversion as function of time of passage of  $H_2$ . ●, Cat I (0.75 g); ×, cat II-blue (0.145 g); gas-velocity  $40 \text{ cm}^3 H_2/\text{min}$ ; pulse size  $2 \text{ cm}^3$ ; rapid succession of propene pulses  $\text{|||||}$ ; He-atmosphere ----.

decay is due to some interaction of  $H_2$  with the catalyst, an interaction that is faster at higher temperatures. This is somewhat surprising because the catalyst had earlier been exposed to hydrogen at  $500^\circ\text{C}$  during its pretreatment.

**2. Reactivation of a deactivated catalyst.** A catalyst was almost completely deactivated by  $H_2$  at  $300^\circ\text{C}$ . Subsequent hereto a stream of  $H_2$  or He was passed over it with the temperature slowly rising. After a treatment at some temperature between 100 and  $450^\circ\text{C}$  the temperature was quickly brought to  $100^\circ\text{C}$  and a pulse of propene injected to test its activity. The results are given in Fig. 2. One can see that above  $300^\circ\text{C}$  the decay process became inverted and the catalyst was reactivated. The reactivation was more complete and faster in He: passing this gas over the inactive catalyst at  $300^\circ\text{C}$  already caused considerable reactivation. Parenthetically, it is worth mentioning that a fully oxidized catalyst ( $Cr^{6+}$ ) cannot be activated by He but only becomes active when exposed to  $H_2$  at  $500^\circ\text{C}$  for 1 hr after which the catalyst was cooled to the desired temperature in He.

The experiments presented here were performed with catalyst I. Catalyst II blue behaved similarly except that the activity of

the  $H_2$  reactivated species was only half that of the He regenerated sample.

**3. Initial activities of various catalysts.** Figure 3 shows initial activities of various types of Cr catalysts with different amounts of Cr, all determined at  $100^\circ\text{C}$ . For the II-type catalysts the degrees of conversion increased steadily with the Cr content with "blue" more active than "green." Catalysts of type I were less active while their increase in activity leveled off when the Cr concentration was still small. Earlier (1) it was concluded from magnetic measurements that "clustering" to small  $Cr_2O_3$

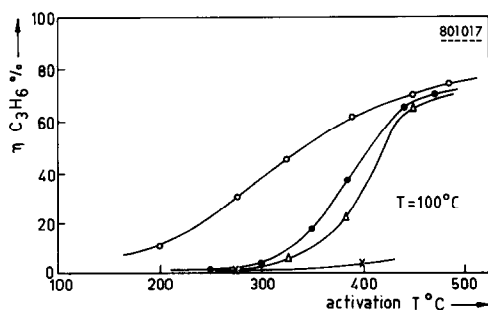


FIG. 2. Reactivation of a deactivated catalyst (I) by passing He or  $H_2$  over it. Reaction conditions, see Fig. 1; activity  $\eta$  determined at  $100^\circ\text{C}$ ; ●, deactivated in  $H_2$  at  $300^\circ\text{C}$  then activated in He at  $T^\circ\text{C}$ ; ○, deactivated in  $H_2$  then activated in  $H_2$ ; △, fresh (= nonreduced) catalyst activated in  $H_2$ ; ×, fresh catalyst treated in He.

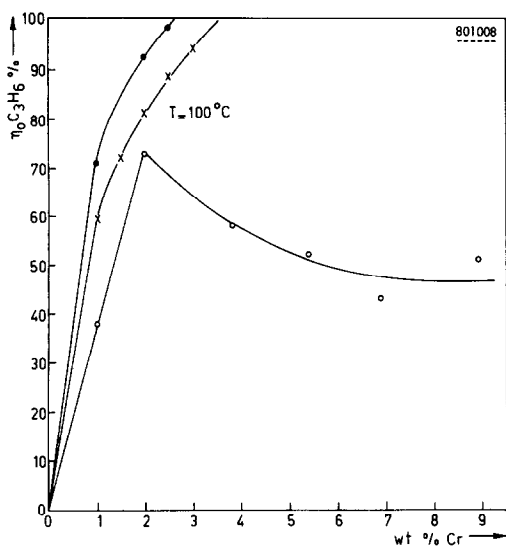


FIG. 3. Initial activity  $\eta_0$  as function of the chromium concentration.  $\circ$ , Cat I (see conditions Fig. 1);  $\times$ , Cat II (0.120 g);  $\bullet$ , Cat II-blue (0.120 g);  $60 \text{ cm}^3 \text{ H}_2/\text{min}$ ; pulse size  $5 \text{ cm}^3$ .

crystals was much stronger developed in catalyst I. It is worth mentioning that the rate of increase of activity with increasing Cr concentration for the II catalysts was probably linear but certainly not quadratic in that concentration. Either therefore all active Cr complexes on the silica contain at least two chromium cations or they possess

one Cr cation but are active contrary to the situation for the  $\text{CrO}_2/\alpha\text{-Al}_2\text{O}_3$  complexes. The spectroscopic evidence given earlier (1) is in favor of the former supposition.

4. The influence of "cycling" on  $\eta_0$  and  $\alpha$ . "Cycling," as explained in the earlier paper (1), is the repeated reoxidation and reduction of a catalyst. Hence,  $n \times$  cycling means that the catalyst has been  $n$  times oxidized to  $500^\circ\text{C}$  and subsequently rereduced with  $\text{H}_2$ . Catalyst I was then exposed to a series of cycle operations ( $n$ ) and tested first at  $100^\circ\text{C}$  and subsequently at  $350^\circ\text{C}$ . In both cases it was reactivated and the experiment repeated. The results are given in Fig. 4;  $a_n$  means "catalyst cycled  $n$  times" and then tested first at  $100^\circ\text{C}$  and after reactivation at  $350^\circ\text{C}$ . Cycling appeared to decrease the tendency to decay at lower temperatures; the initial activity of the catalyst became somewhat smaller at the higher temperatures.

These results indicate that the decay phenomenon is connected with the state of the catalyst and not with the presence of trace inhibitors in the  $\text{H}_2$ .

5. Double pulse experiments: reaction kinetics. To obtain an insight into the kinetics of the hydrogenation, "double pulse" experiments were performed. In these ex-

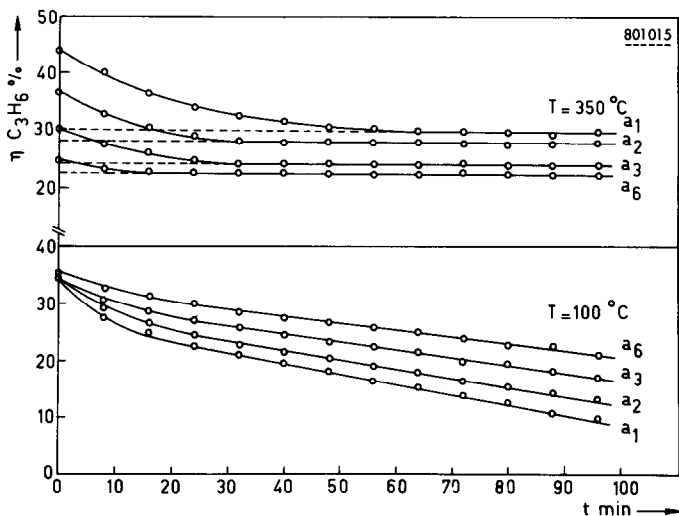


FIG. 4. Influence of cycling on  $\eta_0$  and  $\alpha$  (Eq. (3)). Activities measured at 100 and  $350^\circ\text{C}$ ; Cat II green (0.280 g);  $a_n$  activity after  $n \times$  cycling;  $40 \text{ cm}^3 \text{ H}_2/\text{min}$ ; pulse size  $2 \text{ cm}^3$ .

periments a helium current passed the catalyst in which separate pulses of propene and hydrogen were injected. The distance in time between the two pulses was varied and so was their sequence— $C_3H_6$  first and  $H_2$  later or the reverse. The experiments were performed at  $112^\circ C$ , i.e., in the low-temperature range and at  $450^\circ C$ , a relatively high temperature. The results are given in Fig. 5. If neither of the two gases became adsorbed one might expect the maximum conversion to occur at  $\Delta t = 0$  (where  $\Delta t$  is difference in time between the arrival of the two pulses at the catalyst). If one of the gases were more strongly adsorbed, chromatographic separation would tend to retard its passage through the catalyst so that for maximum conversion the nonadsorbed species should be introduced later. It is immediately obvious from the results at  $112^\circ C$  that the curve "conversion versus  $\Delta t$ " is quite asymmetric: the olefin must have been adsorbed more strongly than  $H_2$ . An entirely different result was observed at  $450^\circ C$ : here the conversion/ $\Delta t$  curve turned out to be symmetric and the maximum activity to be situated near  $\Delta t = 0$ . However, somewhat unexpectedly, another effect be-

came observable here. Even in the absence of  $H_2$  some propene was converted into propane; the catalyst therefore seemed to be a source of hydrogen that became available only at higher temperatures.

A catalyst (II) sample, activated in  $H_2$  and cooled down in He to  $20^\circ C$ , was then used to monitor the reaction between  $D_2$  and 1-butene at  $20^\circ C$ . The D-distribution (MS, "parent peak only" 17.5 kV) was as follows

$$d_0 = 0.5\%; \quad d_1 = 3\%; \\ d_2 = 90\%; \quad d_3 = 6\%.$$

This is entirely in agreement with the results of Burwell *et al.* (4, 18) and Kokes *et al.* (16) for pure  $Cr_2O_3$ ;  $D_2$  from the gas phase is accepted by the olefin with only negligible H/D exchange between either catalyst or olefin with  $D_2$ .

6. *Inhibitors.* Experiments to investigate the inhibitory action of compounds such as  $O_2$ ,  $CO_2$ ,  $H_2O$ , and  $CO$  were performed by pulsing small amounts of the inhibitor over the catalyst after which its activity was determined by pulsing 1-butene over it. Hydrogenation is not the only reaction that

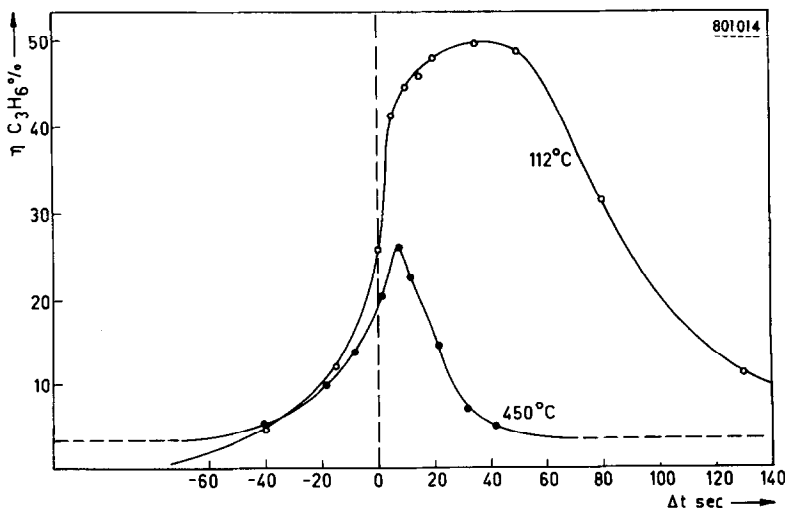


FIG. 5. Double pulse experiments: injection of pulses of  $H_2$  and  $C_3H_6$  in a He-stream. Pulse introduction separated by variable time-interval  $\Delta t$  ( $\Delta t$  positive  $C_3H_6$  first  $H_2$  next; negative reversed sequence);  $\circ$ , conversion at  $112^\circ C$ ;  $\bullet$ , conversion at  $450^\circ C$ ; ---,  $C_3H_6$  conversion at  $450^\circ C$  without  $H_2$  addition.

can occur with this compound; double bond isomerization to *cis*- and *trans*-2-butene can become appreciable. It was observed that there was no correlation between the inhibitory action on the hydrogenation and the isomerization (which did not seem to respond at all). Moreover, isomerization appeared to be a transient phenomenon: after some 10 min passing butene + H<sub>2</sub> over the catalyst, the reaction disappeared. Isomerization therefore is considered to have no connection with the hydrogenation and was ignored in further studies.

O<sub>2</sub> proved to be an inhibitor for the hydrogenation at 20°C but large amounts (in the order of O/Cr = 1) were necessary to completely inhibit all hydrogenation activity. Oxygen poisoning apparently consists in oxidation of Cr in a zone-wise progression of a front through the catalyst.

CO<sub>2</sub> presented an entirely different picture at 20°C: very small quantities in the order of 1 molecule CO<sub>2</sub> per 100 at Cr were already sufficient to completely poison the catalyst.

CO acts in similar quantities but poisoning, although appreciable was not complete

for CO adsorption on CrO<sub>x</sub>/SiO<sub>2</sub> catalysts (see van Reyen *et al.* (12)).

H<sub>2</sub>O added to He acted as an immediate poison for the hydrogenation at 100°C over the II blue catalyst, irrespective of whether it was applied at low (20°C) or high (495°C) temperature. The catalyst changed color and became green-blue (20°C) or green (495°C). If the catalyst was treated subsequently with dry He at 495°C its activity was restored and even increased compared to the original situation (ratio 1.2 for the green-blue catalyst and 1.5–2.2 for the green catalyst, all measured at 100°C). Catalyst II blue, once converted to the green color could not be reduced any more to the blue shade.

The changes in catalyst structure and composition as signaled by its change in activity were also easily observable in the ESR spectra (Fig. 6). If H<sub>2</sub>O was added, the  $\delta$ -signal ( $g = 3.69$ ) disappeared and the  $\beta_1$ -signal ( $g = 1.98$ ) became stronger. Treatment under dry He (causing reactivation of the catalyst) reversed the changes. i.e., the  $\delta$ -signal grew in intensity at the cost of the  $\beta_1$ -signal. It therefore appears that the  $\delta$ -

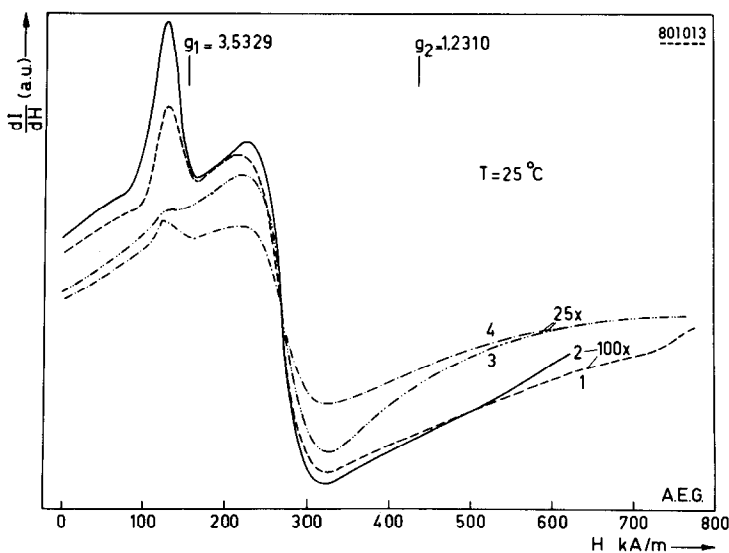


FIG. 6. ESR spectra of Catalyst II (2% wt Cr) after various pretreatments: (1) reduction with H<sub>2</sub> at 495°C (blue); (2) after subsequent activation in dry He at 495°C (blue); (3) hereafter treated with "wet" He at 495°C (green); (4) final treatment with dry He at 495°C (green).



signal is directly connected with the active site.

7. *Catalysts obtained by reduction with CO.* CO was a more potent reduction agent than  $H_2$  and workers such as Krauss who aimed at synthesizing  $Co_x/SiO_2$  containing only Cr(II) always used CO. It was of interest to establish whether Cr(II)/ $SiO_2$  catalysts are active for the hydrogenation of olefins. In one of our attempts to prepare such a catalyst we followed Krauss' recipe (20). The catalyst after calcination was reduced with CO at  $350^\circ C$  and activated by passing an inert gas over it at  $500^\circ C$  (presumably to remove adsorbed CO and/or  $CO_2$ ). This catalyst was only weakly active at  $100^\circ C$  (10% of activity of hydrogen reduced catalyst). An additional pretreatment with  $H_2$  at  $500^\circ C$  did not activate the catalyst for the reaction at  $100^\circ C$ . However, the catalyst proved at least a factor 8 more active at  $400^\circ C$  and for these higher temperatures it appeared just as active as the hydrogen reduced species.

### B. Experiments in the Apparatus with the Gases Circulating over the Catalyst

Most of the experiments to be discussed now were intended to relate the  $H_2/D_2$  equilibration to the olefin hydrogenation. H/D exchange between olefin and  $D_2$  and the interaction of  $D_2$  with the catalyst were also performed in this apparatus.

1. *Exchange of H and D between catalyst and  $D_2$  in the gas phase.* Silica gel heated in  $H_2$  and cooled down in He in the manner as commonly applied in the catalyst pretreatment was exposed to a stream of  $D_2$  or  $H_2 + D_2$  circulating over the sample. After 2–3 hr circulation the gas was analyzed; neither at  $0^\circ C$  nor at  $420^\circ C$  were there more than traces of HD in the gas. Similarly for pure  $D_2$  there was hardly any exchange with H presumably present in the catalyst. The situation was quite different, however, for the  $CrO_x/SiO_2$  catalyst. At  $0^\circ C$  there was an extensive  $H_2/D_2$  equilibration: this will be discussed further on. There was, how-

ever, no exchange of H between catalyst and  $D_2$  in the gas phase. This exchange was found to be extensive at  $420^\circ C$ ; after 2.5 hr the amount of H transferred to the gas phase amounted to 8H per Cr atom. The exchange process was reversible because evacuating the apparatus and refilling with  $H_2$  led after some time to the reappearance of D in the gas phase.

2. *H/D exchange between olefin and  $D_2$ .* In Section A,5 we showed that at temperatures around  $20^\circ C$  the interaction between  $D_2$  and  $C_4H_8$  consisted of a simple addition of  $D_2$  to the double bond without any exchange of H and D between olefin and  $D_2$ . However, as shown in Fig. 7 there is an extensive exchange at  $360^\circ C$ . This figure presents four runs, two at  $0^\circ C$  and two at  $360^\circ C$ . Each pair consists of one run with  $1H_2 + 1D_2 + 3He$  and another with  $1H_2 + 1D_2 + \frac{1}{2}C_3H_6 + \frac{3}{2}He$ . In all cases the "hydrogen" was separated from the hydrocarbons and its H/D ratio determined. The runs at  $0^\circ C$  showed hardly any change irre-

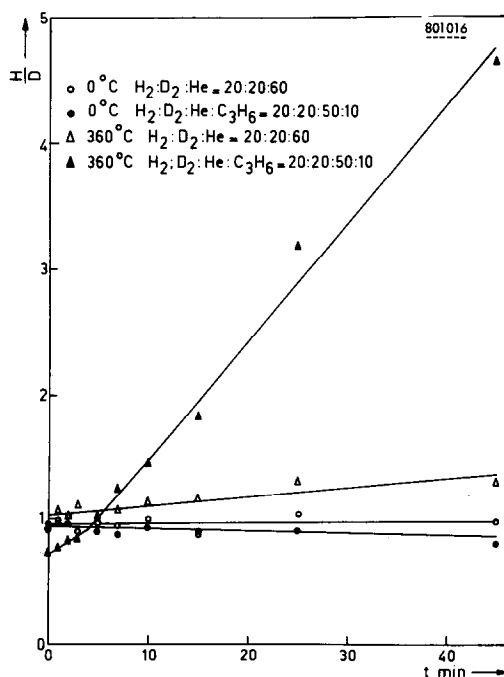


FIG. 7. ( $H_2 + D_2$ ) mixtures circulated over catalyst II (0.510 g) at 0 and  $360^\circ C$  with and without  $C_3H_6$ . H/D ratio in "hydrogen" as function of time of interaction.

spective of whether olefin was or was not present. This confirmed a conclusion made earlier that there is no exchange between hydrogen and olefin at low temperature. The "blank" experiment at 360°C showed a slight increase in the H/D ratio. This was presumably caused by exchange between surface H and gaseous D; although observable it was still small. The run with C<sub>3</sub>H<sub>6</sub>, however, showed a marked rise in H/D, i.e., extensive exchange of H of the olefin and D of the gas phase did occur. A survey of the various reactions in dependence of temperature is given in Table 1.

3. *Similarities between olefin hydrogenation and H<sub>2</sub>/D<sub>2</sub> equilibration.* (a) *Influence of catalyst preparation.* Figure 8 shows that the relative activities of catalysts with a different pretreatment followed similar patterns for olefin hydrogenation and H<sub>2</sub>/D<sub>2</sub> equilibration. The sequence of decreasing activities for catalyst II blue was (reduction in H<sub>2</sub>, activation in He, cooling in He) > (reduction in H<sub>2</sub>, cooling He) > (reduction in H<sub>2</sub>, slowly cooling in H<sub>2</sub>).

(b) *Temperature dependence of rates and of catalyst decay.* For some unknown reason the reproducibility of rate measure-

TABLE I  
Comparison of Hydrogenation, H<sub>2</sub>/D<sub>2</sub> Equilibrium, and H/D Exchange in the Temperature Range 0–500°C

Temperature range (°C)	Hydrogenation	H <sub>2</sub> /D <sub>2</sub> equilibrium	H/D exchange	
			olefin-D <sub>2</sub>	Surface-D <sub>2</sub>
0–100	Fast	Fast	None	None
300–400	Slow	Moderate	Fast	Slow
400–500	Fast	Fast	Fast	Moderate

ments in the range around 200°C was not particularly good, far less so than for the olefin hydrogenation. Rates were found to be high in the 0–100°C range and around 400°C but low around 200°C. Although there is probably some similarity between the temperature dependencies of the two reactions, this is not complete (see also Indovina *et al.* (18)).

(c) *Sensitivity to poisons.* In runs at 0°C over a catalyst with  $3.6 \times 10^{19}$  Cr-atoms, a quantity of CO<sub>2</sub> equivalent to  $4.5 \times 10^{18}$  molecules sufficed to stop the H<sub>2</sub>/D<sub>2</sub> equilibration almost immediately after injection. However, similar amounts of O<sub>2</sub> were al-

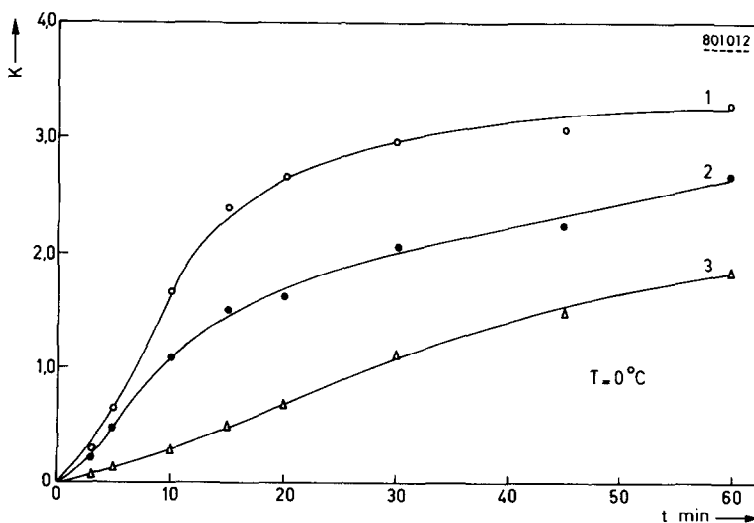


FIG. 8. H<sub>2</sub>/D<sub>2</sub> equilibration by circulation at 0°C over Catalyst II (0.155 g). Influence of catalyst preparation on activity (H<sub>2</sub>:D<sub>2</sub>:He = 1:1:3). All catalyst reduced in H<sub>2</sub> at 450°C hereafter: (1) activated in He at 450°C and cooled to 0°C in He; (2) not activated in He but only cooled to 0°C in He; (3) slowly cooled in H<sub>2</sub>.

most without influence and amounts in the order of  $9 \times 10^{19}$  molecules  $O_2$  were necessary to slow down the rate at the end of the reaction.

4. *Inhibition of the rate of the  $H_2/D_2$  equilibration by olefins.* Figure 9 shows results of runs with and without propene present for  $H_2/D_2$  equilibration at 0 and  $360^\circ C$ . It is fairly obvious that the rates of equilibration became considerably lower in the presence of the olefin. The run at  $0^\circ C$  is particularly informative because the K-time curve is sigmoidal. Propene was adsorbed and blocked sites for the equilibration but in doing so became converted into propane. Consequently, the inhibition decreased later on. It is also of some interest to observe that even at  $360^\circ C$ , where adsorption of propene tended to be negligible (see Section A,5) there still was inhibition.

### C. Once-through Continuous Flow Experiments

1. *Inhibition of  $H_2/D_2$  equilibration by olefins.* The olefin used was  $1-C_4H_8$ , the temperature was  $20^\circ C$ , and catalyst II was used. Mixtures of  $1H_2:1D_2:1X$  (with  $X$  either Ar or  $C_4H_8$ ) were passed at a rate of 30

	$K_1 = \frac{[HD]^2}{[H_2][D_2]}$	$K_2 = \frac{[C_4H_9D]^2}{[C_4H_{10}][C_4H_8D_2]}$
$1H_2:1D_2:1Ar$	3.28	—
$1H_2:1D_2:1C_4H_8$	{ 0.12 0.11	{ 0.13 0.09

$cm^3/min$  over 1.36 g catalyst. The conversion by hydrogenation was 8 to 9%, the isomerization 24%, but the latter reaction disappeared after 10 min. Hereafter the reaction products were assembled and analyzed in the AEI-MS 10 (parent peak). Results, together with those where Ar was used, are given in Table 2.

Again we find that the presence of the olefin inhibits the  $H_2/D_2$  equilibration: the inhibition was quite drastic since in the absence of the olefins the  $H_2/D_2$  equilibration was complete. From  $K_2$  we see that there was no exchange between olefin and  $D_2$ .

2. *Kinetics of the olefin hydrogenation.* Figures 10A and B show the conversion of propene at temperatures varying between 100 and  $400^\circ C$ . The catalyst was II green, the gas ratio  $H_2/C_3 = 4$ , pressure 1 atm,

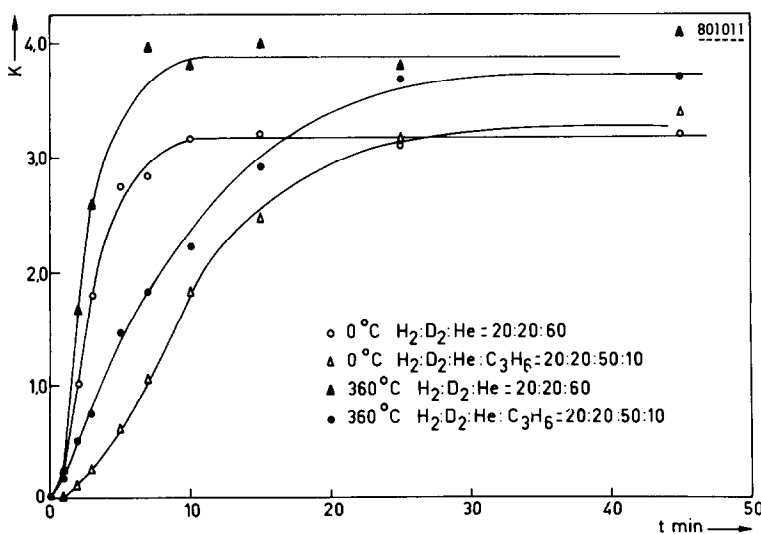


FIG. 9. Influence of the presence of propene on rate of equilibration of  $(H_2 + D_2)$  at 0 and  $360^\circ C$  (Cat II, 0.510 g).

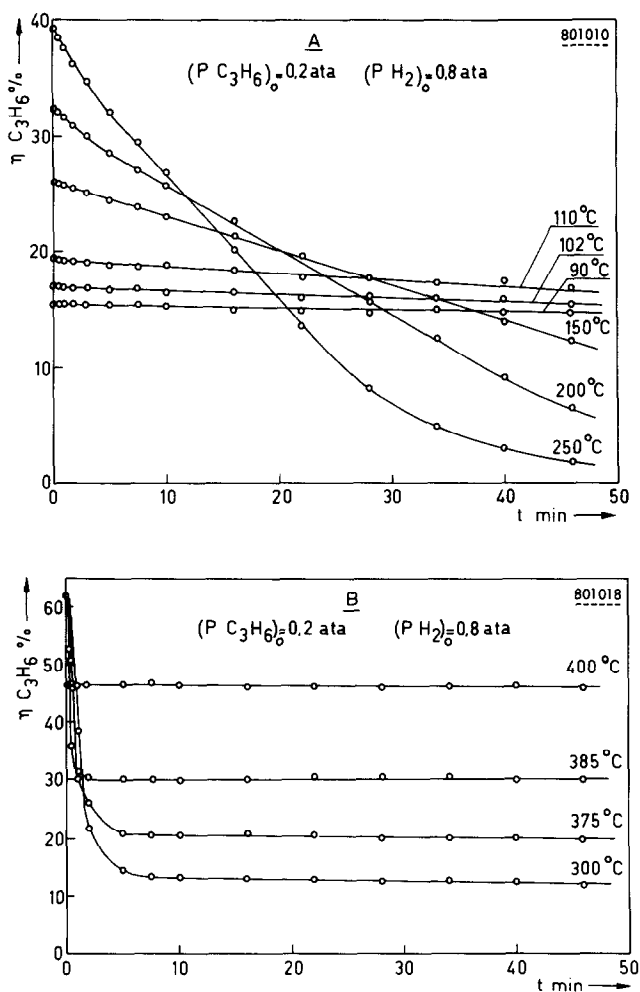


FIG. 10. Rate of hydrogenation of  $C_3H_6$  as function of temperature and run time: (A) temperature range 90–150°C, (B) range 300–400°C. Cat II green (0.280 g), throughput 40  $cm^3$  gas/min.

amount of catalyst 0.280 g, gas velocity 40  $cm^3/min$  (contact time  $\tau_0$  at room temperature about 0.4 sec). The conversion at  $t = 0$  (start of an experiment) increased with temperature but only slowly. The rate of decay of catalyst activity increased more rapidly. It should be noted that the rate of decay in these experiments was very similar to that discussed earlier for the pulse experiments (Fig. 1); therefore it must be due to an interaction of  $H_2$  with the catalyst. Above 300°C the decay reaction became very fast but it did not lead to complete deactivation. Instead, a level of constant activity devel-

oped; the height of the level increased with temperature. For reasons of convenience we shall refer to the reaction below 300°C as the *L(ow)-T(emperature) R(eaction)* = *LTR*, and to that above 300°C as *H(igh)-T(R)* = *HTR*.

The kinetics of the LTR at 100°C can be derived from experiments shown in Figs. 11A and B. The rate was linear in the partial hydrogen pressure ( $p_H$ ); it increased with the olefin partial pressure ( $p_C$ ) up to a certain maximum value and remained constant at higher  $p_C$ . This suggests that each catalytic site contains two moieties, one that

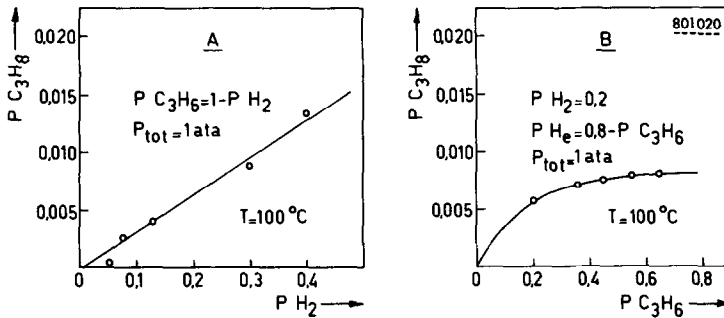


FIG. 11. Kinetics of hydrogenation at 100°C as a function of partial pressures of propene (B) and hydrogen (A). Cat II green (0.100 g); throughput 40 cm<sup>3</sup>/min.

adsorbs H<sub>2</sub> and the other the olefin. Writing for the partial pressures at the reactor inlet  $p_C^i$  and  $p_H^i$ , the equation becomes:

$$-\frac{d(p_C/p_C^i)}{d\tau} = k_L \cdot \frac{p_H}{p_H^0 + p_H} \cdot \frac{p_C}{p_C^0 + p_C} \quad (4)$$

where  $k_L$  is the reaction constant for the surface reaction and  $p_H^0$ ,  $p_C^0$  are equilibrium pressures for half coverage of the two sites. Since  $p_H$  seems to be large (see Fig. 12), the rate equation can be written as:

$$\frac{d(p_C/p_C^i)}{d\tau} = k_L \frac{p_H}{p_H^0} \cdot \frac{p_C}{p_C^0 + p_C} \quad (5)$$

Integration gives:

$$-\ln(1 - \eta) + \left(\frac{p_C^i}{p_C^0}\right) = k_L \left(\frac{p_H}{p_H^0}\right) \left(\frac{p_C^i}{p_C^0}\right) \cdot \tau \quad (6)$$

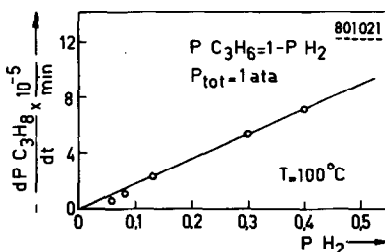


FIG. 12. Dependence of rate of decay on the hydrogen partial pressure at 100°C. Rate of decay is first order in hydrogen. Cat II green (0.100 g); throughput 40 cm<sup>3</sup>/min.

We note that  $p_C^i = 0.2$  atm, while  $p_H$  remained approximately constant at  $p_H^i = 0.8$  atm. The contact time  $\tau$  depended on the temperature but this was approximately counteracted by the fact that  $k$  contains the ratio  $N_{cat}/n_C^i$ , i.e., the ratio of numbers of catalytic sites per unit of volume ( $N_{cat}$ ) to the number of olefin molecules at unit volume ( $n_C^i$ ) at the inlet of the reactor. So we write  $\tau = \tau_0$ .

There are not enough data to adequately fit Eq. (6) so we try the simplified versions: for  $p_C^i/p_C^0 \ll 1$ :

$$-\ln(1 - \eta) = k_L \frac{p_H^i}{p_H^0} \cdot \frac{p_C^i}{p_C^0} \cdot \tau = k_L' \tau_0 \quad (6a)$$

for  $p_C^i/p_C^0 \gg 1$ :

$$\eta = k_L \frac{p_H^i}{p_H^0} \cdot \tau = k_L' \tau_0 \quad (6b)$$

Plotting  $\ln k_L'$  (resp.  $\ln k_L''$ ) versus  $1000/T$ :

$$\ln(-\ln(1 - \eta_0)) = -1.283 \cdot 1000/T + 1.779 \quad (7a)$$

(six experiments; corr. coeff. = 0.997)

$$\ln \eta_0 = -1.099 \cdot 1000/T + 1.196 \quad (7b)$$

(six experiments; corr. coeff. = 0.996)

The data do not allow a choice between the two. Since we expect to have to extrapolate later on to the high-temperature range where Eq. (7b) is probably less adequate we select Eq. (7a). Note that for both cases we find an "activation energy" that is surpris-

ingly low (7a, 2.55 kcal = 10.7 kJ; 7b, 2.20 kcal = 9.1 kJ) and of the order of  $kT$ .

The decay can be assumed to arise from a reaction ( $S$  is site)



Therefore, since  $p_{\text{H}}$  is approximately constant (0.8 atm.):

$$-\frac{1}{t} \ln \frac{\ln(1 - \eta_t)}{\ln(1 - \eta_0)} = k_d \cdot p_{\text{H}} = k'_d \quad (9)$$

where  $t$  = run time (time in seconds after start of experiment),  $\eta_t$  the conversion at  $t$ ,  $\eta_0$  the conversion at  $t = 0$ . Plotting  $\ln k'_d$  versus  $1/T$  we obtain:

$$\ln k'_d = 3.07 - 4.98 \frac{1000}{T} \quad (10)$$

(six experiments corr. coeff. = 0.98)

The kinetics of the HTR can be found from Figs. 13A and B. In good agreement with Denisova *et al.* (16) we find that the rate of hydrogenation at 300°C was first order in the partial pressure of propene but of lower order in the partial pressure of hydrogen being even of zero-order at  $p_{\text{H}} = 0.8$ . For the HTR a more appropriate kinetical expression would then be:

$$-\frac{d(p_{\text{C}}/p_{\text{C}}^0)}{d\tau} = k_{\text{H}} \cdot \frac{p_{\text{H}}}{p_{\text{H}}^0 + p_{\text{H}}} \cdot \frac{p_{\text{C}}}{p_{\text{C}}^0} \quad (11)$$

However, as we shall show later, the equilibrium pressures  $p_{\text{H}}^0$  in Eq. (5) and  $p_{\text{H}}^0$  in Eq. (11) do not refer to the same adsorption process. The former is connected to the

weak heterolytic adsorption, the latter to a homolytic reduction of  $\text{Cr}^{3+}$  to  $\text{Cr}^{2+}$ .

The surprisingly low activation energies calculated for the LTR might invoke the criticism that its rate is determined by diffusion. However, a comparison of conversions with the smaller and larger catalyst particles did not reveal significant differences. The routine check with help of the Thiele modulus (see for instance Smith (21)) showed this number to be 1/30; diffusional mass transport as a rate-determining factor can therefore be excluded, at least as far as regards the reactants and products.

#### DISCUSSION

We shall attempt in the following to arrive at a semiquantitative model for the composition and structure of the  $\text{CrO}_x/\text{silica}$  surface. Since there are some apparently conflicting observations in this connection, it will be useful to start with a short review of the reactions that lead to the formation of the various complexes on this surface.

The structure of solid  $\text{CrO}_3$  consists of chains of tetrahedral  $[\text{Cr}^{\text{VI}}\text{O}_4]$  groups linked together by the sharing of two of the four apices; there is not much interaction between the chains (25). We write the structure as  $[-\text{CrO}_2-\text{O}]_n$ , with  $n$  a large integer. When solved in water Cr-O-Cr bonds become hydrolyzed under formation of terminal OH groups

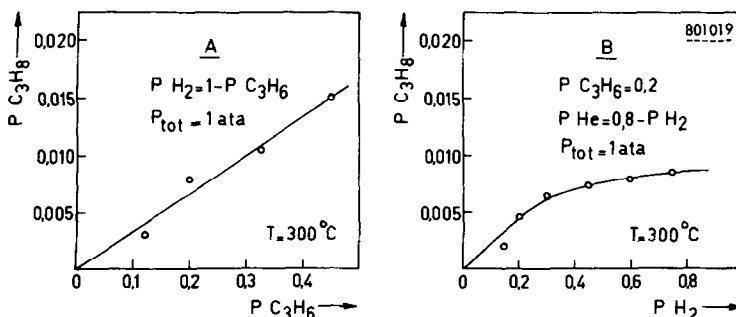
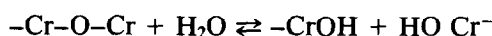


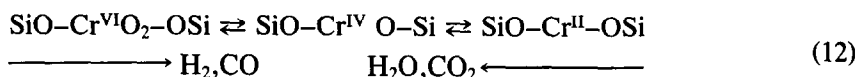
FIG. 13. Kinetics of hydrogenation at 300°C as a function of partial pressures of propene (A) and hydrogen (B).

This process can ultimately lead to the formation of small molecules such as bichromates  $\text{HO-CrO}_2\text{-O-CrO}_2\text{OH}$  and chromates  $\text{HO-CrO}_2\text{-OH}$ . It is generally assumed (22, 23) that the concentration of species larger than bichromates is relatively low.

When a solution of  $\text{CrO}_3$  reacts with a silica surface that is presumed to have its maximal coverage of silanol groups, its Cr complexes become bonded to this surface by  $\text{Si-O-Cr}$  bonds; ion-exchange catalysts of type II can be assumed to be formed according to this pattern (1). We concluded that there was a considerable amount of bichromate on the surface, a conclusion based on the observation that the uv-Vis spectrum of the catalyst showed a band at  $20,500\text{ cm}^{-1}$  that was also observable in the spectrum of  $\text{K}_2\text{Cr}_2\text{O}_7$  but not in that of the  $\text{K}_2\text{CrO}_4$  spectrum. MacDaniel (24), on the

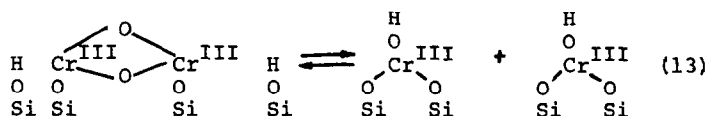
other hand, from measurements on the decrease in number of silanol groups as a consequence of the introduction of Cr, concluded that there were only single Cr complexes present, each bonded to the surface by two  $\text{Si-O-Cr}$  bridges. In the following discussion we shall assume that there are only two types of complexes on the surface, single Cr complexes (chromates) and binuclear species (dichromates). Both types will be assumed to be anchored to the surface by two bridges. Our problem is now to decide the ratio between the two types. We shall attempt to find the answer to this problem from information (ESR, magnetic susceptibility, see Ref. (1)) obtained after reduction by  $\text{H}_2$  or  $\text{CO}$ .

As readily seen from Eq. (12), reduction of single Cr complexes by  $\text{H}_2$  or  $\text{CO}$ , can only result in Cr with even valencies, IV or II:



Dichromates, on the other hand, can be expected to give all Cr valencies from VI to II including the odd valencies. Since, under the circumstances of the reduction, it is reasonably certain that only  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{II}}$  will remain present and because we found con-

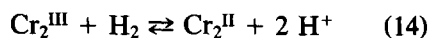
siderable amounts of  $\text{Cr}^{\text{III}}$  it appears that our catalyst samples contained or had contained binuclear complexes. Evidently, this does not necessarily mean that the binuclear species were still there because there could always be a reaction as given in (13)



However, we propose that the deactivation of the catalyst in the presence of  $\text{H}_2$  was caused by a reduction of the catalyst, a reduction that could hardly be else than from  $\text{Cr}^{\text{III}}$  to  $\text{Cr}^{\text{II}}$ . We also showed that there is an activated adsorption of  $\text{H}_2$  that occurs in the same temperature range as that where the rate of deactivation is appreciable. We

therefore conclude that:

(a) The species on the surface that is the active catalyst and that is susceptible to become deactivated by  $\text{H}_2$  is the binuclear  $\text{Cr}^{\text{III}}$  complex.

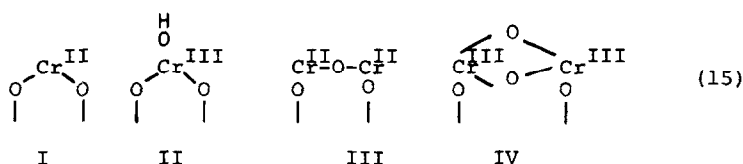


(b) In good agreement with Burwell, that

only Cr<sup>III</sup> is active for the olefin hydrogenation.

These conclusions do not necessarily mean that only binuclear Cr<sup>III</sup> complexes can be active. Burwell's mechanism for the hydrogenation only demands that there is one Cr<sup>III</sup> with at least one anion-vacancy and one oxygen to accept a proton. Since a single Cr<sup>III</sup> cannot be reduced by hydrogen, a single Cr<sup>III</sup> complex should be immune against deactivation. It is in this connection that the results of the "cycling" experi-

ments illustrated in Fig. 4 gain importance. They showed that "cycling" tended to decrease the deactivation of the catalyst without, however, influencing its initial activity. The explanation can be given on the basis of the reactions shown in Eq. (13); "cycling" apparently tends to dissociate binary complexes into single Cr species. A catalyst that has been frequently regenerated by reoxidation probably contains all four species given in (15).



Catalyst samples as usually applied by us, that is, without "cycling," contained only I and IV and after the deactivation I and III. We observed indeed that after deactivation all activity had disappeared so all Cr<sup>III</sup> should be Cr<sub>2</sub><sup>III</sup>. Wittgen *et al.* give the maximal "high-temperature" adsorption of H<sub>2</sub> (Table 1) as being equal to 1.0 cm<sup>3</sup>/g for a catalyst containing 2 wt% Cr. The H/Cr ratio accordingly should be 0.22; about 20% of all Cr was present in the form of the binuclear species. It should be noted that this was all the Cr catalytically active for the hydrogenation, exchange, and equilibration reactions.

In retrospect, from the point of view of the number of Cr per surface complex, McDaniel's and our results therefore do not appear to be as different as believed earlier. McDaniel reports an OH/Cr ratio of 2 while our data average at 1.8. There was enough dichromate present to account for the observation of the 20,500 cm<sup>-1</sup> band while at the same time it becomes possible to account for the large amounts of Cr<sup>II</sup> in the blue catalyst samples; these were derived from the chromate species originally present.

It is instructive to make a model of the catalyst surface structure based on these and other data. To do so, we start from Peri's model of a silica surface with a maximal OH coverage of about 4.5/nm<sup>2</sup> (26). Our catalyst with 2 wt% Cr and a surface area of 600 m<sup>2</sup>/g had a Cr density of 0.385 Cr/nm<sup>2</sup> of which 0.30 Cr was in single complexes and 0.085 Cr in binuclear species. It was reduced in H<sub>2</sub> at around 500°C and cooled in He; on the basis of McDaniel's data a free silica surface would then have 1.5 OH/nm<sup>2</sup>. After taking into account the Cr present there should remain 1.27 OH/nm<sup>2</sup> and the ratio of H(silanol)/Cr would be 3.3. However, the H/D exchange results given on p. 368 gave 8 H per Cr, indeed a major discrepancy. There are obviously two ways to correct the theory, either we allow more silanol groups on the silica surface or we add H<sub>2</sub>O ligands to the Cr cations. The first leads to a silanol coverage of 80% of all available sites while the second adds on the average 2.35 molecules water to each Cr. When we add two H<sub>2</sub>O to every Cr<sup>II</sup> to give it a square planar surrounding and three H<sub>2</sub>O to every Cr<sup>III</sup> to make it octahedrally surrounded we arrive at a total



number of H<sub>2</sub>O per Cr equal to 2.22. The actual situation might be intermediate between the two corrections; it is clear, however, that the bulk of the catalyst contains much water, too much probably to allow enough ligand vacancies on the majority of the Cr<sup>III</sup> cations to allow catalysis. The observation that only 1% of All Cr was active, since only one CO<sub>2</sub> per 100 Cr sufficed to completely poison the catalyst, fits well in this picture. It also explains the ESR results; Fig. 6 shows that the  $\delta$ -signal for Cr<sup>III</sup> ( $g = 3.69$ ), that becomes observable when the catalyst was treated in dry He at 495°C, was immediately eliminated when moist He was passed over the catalyst. The concentration of the species that gave rise to this signal was estimated at about 0.8% of all Cr (Ref. (1), Table 2), in fair agreement with the result of the poisoning by CO<sub>2</sub>. We thus conclude that the active site was a Cr<sup>III</sup> cation that occurred only in small amounts. It is commonly accepted (27) that the  $\delta$ -signal represents magnetically isolated Cr<sup>III</sup>, a description that would fit the structural situation of Cr<sup>III</sup> cations in small clusters with each Cr being present in a state of lower symmetry thereby precluding antiferromagnetic interaction. Such a state might presumably arise if ligands were removed from the central cation.

Let us make a somewhat more detailed model of surface compound IV, starting from the model proposed by Stone and Vickermann (15). It consists of two Cr<sup>3+</sup> cations that are octahedrally surrounded by oxygens; the two octahedra share a face. This complex will become attached to the silica surface via its two apex oxygens farthest part (2 and 3, Fig. 14). Bond lengths and bond angles applied were derived from Wells (25) viz.: Cr<sup>3+</sup>-O = 2.04 Å (radius Cr<sup>3+</sup> = 0.64 Å, radius O<sup>2-</sup> = 1.40 Å); Si-O = 1.60 Å; bond angle Si-O-Si = 146°; nearest distance Si---Si = 3.08 Å.

The Si-O-Cr angle becomes equal to 115°, which is near enough to the tetrahedral angle to make the model almost strainless. Each Cr<sup>3+</sup> has three oxygen neighbors

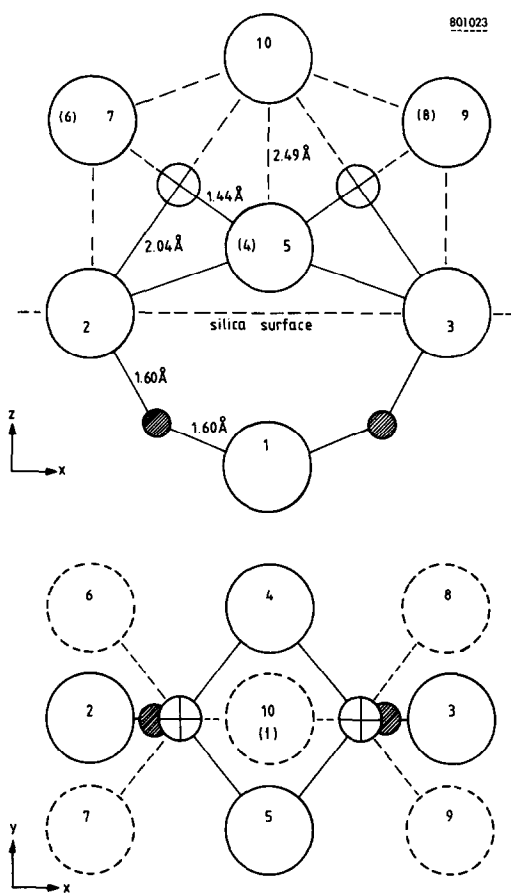


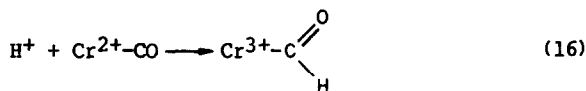
FIG. 14. Model for binary Cr<sup>3+</sup> complex anchored to the silica surface. ●, Si-atom; ○, oxygen atom; ⊕, chromium atom.

that are bridging viz.: O<sub>2</sub> (or O<sub>3</sub>), O<sub>4</sub> and O<sub>5</sub>; this makes the complex electrically neutral. Evidently, leaving all the remaining ligand positions empty would create an energetically unfavorable situation; the other positions can be filled with neutral ligands such as H<sub>2</sub>O. To make the complex catalytically active, however, at least two of the ligand positions should remain empty. Infrared evidence has been given by Borello and Zecchina (28) and by Peri (29) (see also Burwell (8) that Cr<sup>3+</sup> of CN = 4 exists). However, Cr<sub>2</sub><sup>3+</sup> complexes are in a better position than single Cr<sup>3+</sup> species because they can have two vacancies per two Cr<sup>3+</sup>, sufficient to become catalytically active but energetically more attractive. This might be

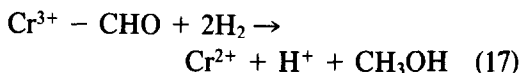
another reason for the dominant position of  $\text{Cr}_2^{3+}$  complexes in our considerations.

An observation that remains to be explained concerns catalysts reduced with CO, usually a more powerful agent when requiring deep reduction. As reported earlier (1) CO reduction does not only reduces Cr cations but also dehydrates the silica surface because of migration of silanol groups to the reduced Cr cations. These become reoxidized by water from the silanol under formation of  $\text{H}_2$  and are subsequently reduced again to  $\text{Cr}^{\text{II}}$ . We found that a catalyst reduced with CO proved inactive at  $100^\circ\text{C}$  as was expected because all Cr was

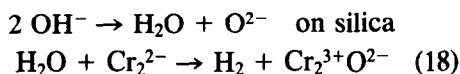
reduced to the divalent state. However, it remained inactive when heated under He at  $495^\circ\text{C}$ , a treatment that used to revive catalysts reduced by  $\text{H}_2$ . Krauss *et al.* (20) showed earlier that the treatment also suffices to remove adsorbed CO. Still another possibility was that the reduction by CO failed to deliver enough OH on the surface to accomplish reoxidation. However, we found that the catalyst could be revived by a  $\text{H}_2$  treatment at  $495^\circ\text{C}$ . A tentative explanation for this phenomenon might be that the species adsorbed to Cr is not CO but a formyl radical, formed by interaction of a silanol H with an adsorbed CO



The interaction with  $\text{H}_2$  can now be surmised to form methylalcohol



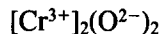
and the  $\text{Cr}^{2+}$  cation can be reoxidized again by interaction with OH



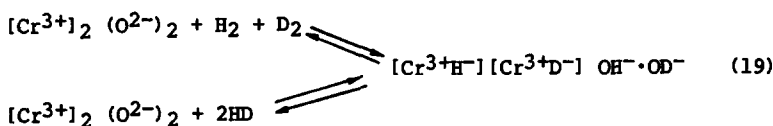
All these observations add up to the impression that the behavior of our  $\text{CrO}_x/\text{SiO}_2$  catalysts was strongly influenced by the silanol groups on the support. It might be surmised that these interactions became so visible because of the extreme properties of the support such as a large surface area, a

relatively small pore volume with as a consequence a small pore diameter, and difficult migration of  $\text{H}_2\text{O}$ .

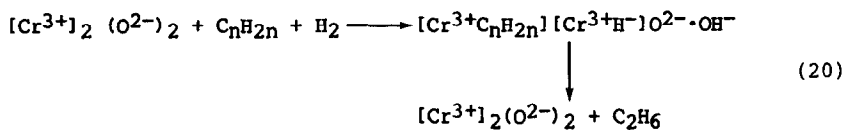
A discussion of the kinetics would be somewhat cumbersome when using this structural model; let us therefore simplify it again by writing it as:



where  $[\text{Cr}^{3+}]$  is a surface  $\text{Cr}^{3+}$  cation next to a surface vacancy [ ] and the  $\text{O}^{2-}$  anions are bridging between the two  $\text{Cr}^{3+}$ . We omit the bridges to the surface at this point but will later on introduce them again; for the description of the reactions at temperatures below  $150^\circ\text{C}$  we do not need them. The  $\text{H}_2/\text{D}_2$  equilibration in this temperature range can then be represented by:



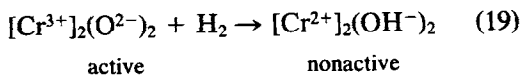
and the olefin hydrogenation under the same circumstances by:



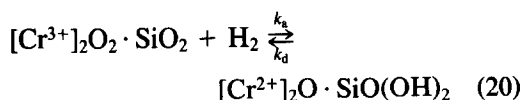
(An atom or molecule placed within the brackets next to a  $\text{Cr}^{3+}$  cation signifies that it is bonded to the cation while accommodated into the anion vacancy.) We assume that the olefin is connected to the cation by  $\sigma\pi$ -acceptor bonding. Note that the presence of an olefin should inhibit the  $\text{H}_2/\text{D}_2$  equilibration as indeed we found experimentally. However, in the presence of an excess of olefin this should also inhibit its own hydrogenation, and so far we have not been able to confirm this. Indeed, the absence of this inhibition suggests that the two vacancies are not identical and that only one of the two can adsorb the olefin.

The explanation appears simple. The anion vacancies (ligand vacancies) have to accept olefin and hydride ions; there does not appear to be symmetry restrictions to house the hydride ion in either the 6–9 set or in the bridging 10-position. However, if we assume that the olefin is  $\sigma\pi$ -double bonded when adsorbed to Cr, the 10-position is probably less suitable. This suggests that the olefin never can occupy the 10-position so that, independent of its partial pressure, the 10-position remains available for the hydride ion.

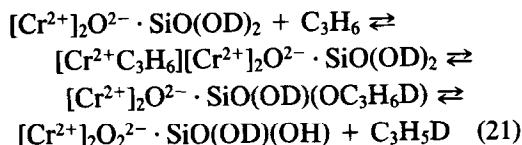
The mechanism for the reactions  $>300^\circ\text{C}$  (HTR reactions) is less obvious. We know that the deactivation of the site for the reactions  $<150^\circ\text{C}$  (LTR reactions) occurs by an interaction with  $\text{H}_2$ ; so we conclude that the high-temperature hydrogen adsorption is closely connected with the catalyst decay, for instance



We also know that in this temperature range ( $350\text{--}500^\circ\text{C}$ ) there is a considerable interchange (“spillover”) of  $\text{H}_2$  adsorbed via Cr and of H from the silanol groups. The adsorption–desorption reactions of  $\text{H}_2$  on  $\text{CrO}_x/\text{SiO}_2$  therefore are not limited to the Cr cations and their ligands but also involve the silanol groups; we need the Si–O–Cr bridges to allow transfer of H to and from the silica surface. We write this symbolically as:



i.e., we consider it essential for the binary complex to be bonded to the silica surface in order that the reduction of  $\text{Cr}^{3+}$  and the hydration of the silica surface can occur as a concerted reaction. The consequence of this model is that HTR and LTR are basically the same reaction. The experiments shown in Fig. 2 furnish the proof that this is true: the genesis of the HTR proceeds parallel with revival of the LTR. The two reactions differ, however, in one point. The HTR shows H/D exchange between  $\text{D}_2$  and olefin; this is lacking in the LTR. We ascribe this to the reaction:



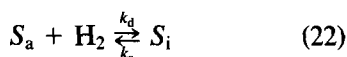
Such an interaction with  $1\text{-C}_4\text{H}_8$  as the olefin would undoubtedly lead to double bond isomerization.

The numerical data of Figs. 10A and B (Section C,2, kinetics of the olefin hydroge-

nation) can then be used to make an estimate of the heat of adsorption and the activation energy of adsorption for H<sub>2</sub>. We assume that equation

$$\ln(-\ln(1 - \eta_0)) = 1.779 - 1.283 \cdot 1000/T \quad (7a)$$

can be extrapolated over a whole range of temperatures for the "clean" surface. From the equation



where S<sub>a</sub> is an active and S<sub>i</sub> an inactive (reduced) site, the fraction of active sites at time *t* can be calculated as

$$\theta_t = \frac{\ln(1 - \eta_t)}{\ln(1 - \eta_0)} \quad (23)$$

During the run

$$-\frac{d\theta_t}{dt} = k_d p_H \cdot \theta - k_a(1 - \theta) \quad (24)$$

Since *p<sub>H</sub>* is approximately constant at 0.8 atm, we write *k<sub>d</sub>p<sub>H</sub>* = *k'<sub>d</sub>*. After integration

$$\theta_t = \frac{k_a}{k_a + k'_d} \{1 - \exp[-(k_a + k'_d)t]\} + \exp[-(k_a + k'_d)t] \quad (25)$$

At run-times tending to infinity we get

$$\theta_t = \theta_{eq} = \frac{k_a}{k_a + k'_d p_H} = \frac{k_a}{k_a + k'_d} \quad (26)$$

We assume that conversions from 250°C upward and *t* = 2400 sec are related to the equilibrium condition. Since  $\eta_0$  can be computed from Eq. (7a), and  $\theta_{eq}$  from the steady-state level we find

$$\ln\left(\frac{k'_d}{k_a}\right) = -11.32 + 7.52 \frac{1000}{T} \quad (27)$$

(5 exp., corr. coeff. = 0.92)

The decay data for temperatures from 250°C downward are given by

$$\ln k'_d = 3.07 - 4.98 \frac{1000}{T} \quad (10)$$

Combining (26) and (10) we find

$$\ln k_a = 14.39 - 12.50 \frac{1000}{T} \quad (28)$$

The result of these calculations is that the reduction of the binary trivalent complex to the bivalent one has an (exothermic) enthalpy of -14.9 kcal (62.5 kJ mol<sup>-1</sup>). The activation energy of *k<sub>d</sub>* ~ 10 kcal (42 kJ mol<sup>-1</sup>), that of *k<sub>a</sub>* ~ 25 kcal (100 kJ mol<sup>-1</sup>). The numerical data of Eqs. (7a), (10), (27), and (28) allow a simulation of the curves of Figs. 10A and B. This is illustrated in Fig. 15; the agreement seems satisfactory.

We still have to describe the HTR kinetics from this model. Evidently, its reaction constant is *k<sub>L</sub>* ·  $\theta_{eq}$ . With  $\theta_{eq} = \pi_H^0 / (\pi_H^0 + p_H)$  where  $\pi_H^0 = k_a/k_d$  and the assumption *p<sub>C</sub><sup>0</sup>* ≫ *p<sub>C</sub>*, we can rewrite Eq. (5) for high temperatures:

$$\begin{aligned} \frac{d(p_C/p_C^0)}{dt} &= k_L \cdot \frac{\pi_H^0}{\pi_H^0 + p_H} \cdot \frac{p_H}{p_H^0} \cdot \frac{p_C}{p_C^0} \\ &= k_L \frac{\pi^0}{p_H^0} \frac{p_H}{\pi_H^0 + p_H} \frac{p_C}{p_C^0} \end{aligned}$$

which is similar to Eq. (11) with *k<sub>H</sub>* = *k<sub>L</sub>*  $\pi_H^0 / p_H^0$ . Note that  $\pi_H^0 \neq p_H^0$ ; the first relates to the reductive homolytic adsorption, the second to the heterolytic adsorption.

## CONCLUSIONS

The preceding discussion showed that there exists a strong interaction in the CrO<sub>x</sub>/SiO<sub>2</sub> catalyst between the CrO<sub>x</sub> catalyst and its silica support, an interaction that is developed at its strongest in the ion-exchange (catalyst II) species. Here, the active component is predominantly present in the form of Cr complexes bound ("immobilized") to the silica by surface Si-O-Cr bonds. To become active the Cr<sub>*n*</sub> complexes (with 1 ≤ *n* ≤ small number such as two) may have to undergo a pretreatment such as reduction by H<sub>2</sub> or CO. For reactions such as the hydrogenation of olefins the preferred valency is Cr<sup>III</sup> (Burwell). Exhaustively reduced catalysts where Cr<sup>II</sup> is the preponderant species are inactive for this reaction as we showed in the preceding pages.

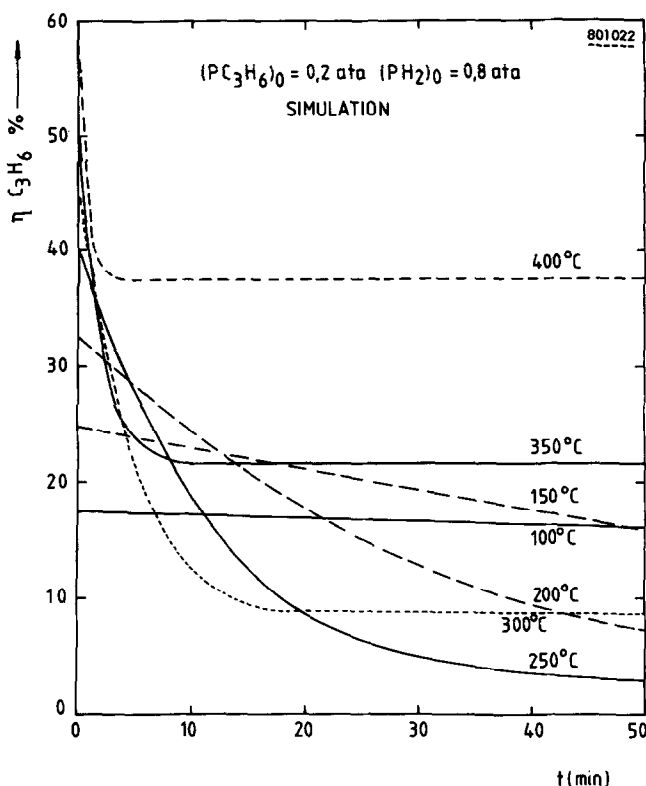


FIG. 15. Simulation of the curves of Figs. 10A and B based on the numerical data of Eqs. (7a), (10), (27), and (28).

Burwell's mechanism for reactions as given above requires two empty ligand sites on the  $\text{Cr}^{\text{III}}$ , one to accept a hydride ion from the heterolytic dissociation of  $\text{H}_2$  and another to provisionally bind the olefin by  $\sigma\pi$ -backbonding. The actual CN of active  $\text{Cr}^{\text{III}}$  then should be 4.

The silica support has silanol groups on its surface. Calcination in a dry atmosphere at elevated temperatures will remove silanol groups, a reaction that is slow because of the activated migration of  $\text{H}_2\text{O}$  through the pores, respectively OH over the surface. Reduction by  $\text{H}_2$  will tend to increase the OH concentration. They can interfere in several ways with the action of the catalyst complexes. Inactive  $\text{Cr}^{\text{II}}$  complexes can be reoxidized and the catalyst reactivated but empty ligand sites on  $\text{Cr}^{\text{III}}$  complexes can be blocked, which leads to deactivation of the catalyst. Evidence for

both processes has been given in this paper. A third type of interaction has to do with changing the degree of clustering of the Cr complexes; increasing their number will tend to decrease the number of Cr per cluster ultimately producing single Cr complexes, while removing silanol groups will increase the size of the clusters. This effect is of some importance because single Cr complexes are restricted in the way they can change their valencies;  $\text{Cr}^{\text{II}}$  when interacting with  $\text{H}_2\text{O}$  can give only  $\text{Cr}^{\text{IV}}$  (which is energetically unfavorable) while  $\text{Cr}_2^{\text{II}}$  can give  $\text{Cr}_2^{\text{III}}$ . Moreover, since two neighboring anion vacancies are required by the reaction mechanism, it is probably energetically more difficult to dissociate two  $\text{H}_2\text{O}$  molecules from one  $\text{Cr}^{\text{III}}$  than from a binuclear cluster. In the first case two out of six ligands have to be removed and in the second case two out of 10 ligands.

The combination of these interactions will produce a complicated situation in which the final outcome will depend on the one hand on the properties of the support (surface area/g, pore volume in  $\text{cm}^{-1}/\text{g}$ , the two determining the average pore diameter and the particle size of the applied catalyst) and on the other hand on details in the preparation (calcination temperature, the rate of temperature increase, and the velocity of the reducing gas during the reduction). The silica support used in this study was probably somewhat exceptional in this connection. It had a large surface area ( $600 \text{ m}^2/\text{g}$ ) which enabled a large concentration of Cr complexes per unit volume. On the other hand, its pore volume was quite low (0.4) which made it difficult to dehydrate because the pore diameter was on the average very low ( $15 \text{ \AA}$ ). One consequence was that the deactivation-reativation phenomenon became particularly visible; another that only catalyst complexes located at or near the periphery of the catalyst particle were active.

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