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Hydrogen-Deuterium Exchange in Saturated Hydrocarbons on α-Chromia Catalyst

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The kinetics of hydrogen–deuterium exchange in methane, ethane, and propane have been studied with unsupported α-chromia as catalyst in the temperature range of 598–688°K. The apparent activation energies for methane, ethane, and propane are 88, 130, and 84 kJ mol^{-1}, respectively, similar to those found on chromia gel. The order of reaction with respect to hydrocarbons and deuterium has been determined as also having the kinetic isotope effect. The main initial products are CH_3D and CD_4 with methane, $C_2H_4D_2$ and C_2D_6 with ethane, and C_3H_7D and C_3D_8 with propane. A change in product distribution as a function of temperature, conversion, aging, and oxygen–deuterium treatment has been observed. In agreement with the kinetic data and the effect of oxygen, Cr^{3+} has been assumed as the active species of the chromia catalyst, whereas Cr^{2+} is an inactive site on the surface. There is no direct proof that chromium ion in a valence state higher than 3+ plays an important role in the exchange reaction. It was established that dual Cr^{3+}–Cr^{3+} sites are responsible for the formation of ethane-d_2. After a long deuterium treatment the number of dual sites is decreased, the effect being revealed in the decreased rate of exchange and the small amount of ethane-d_2. On the contrary, the formation of methane-d_4 is interpreted by the formation of Cr=C bonds by analogy with homogeneous complexes. In the case of propane, the exchange reaction can be adequately interpreted by a π-allyl mechanism.

INTRODUCTION

Hydrogen–deuterium exchange reactions in various hydrocarbons have been extensively investigated using chromia gel as catalyst (*1–6*). It has been established that chromia gel is fairly stable when activated in helium up to 743°K, and its activity increases with the activation temperature. On this catalyst, hydrogen atoms attached to the primary carbon atoms of a saturated hydrocarbon molecule can be exchanged about six times faster than those bonded to secondary carbon atoms. In regard to activation energies, a maximum has been shown for ethane, measured in a temperature range between 623 and 823°K.

The second characteristic feature of deuterium exchange in hydrocarbons is the distribution of species containing different numbers of deuterium atoms in the molecule. Although Burwell and co-workers (*1–6*) did not make detailed kinetic investigations their works clearly indicate that the main product of exchange is hydrocarbon with one deuterium atom. Multiple exchange leading to the formation of perdeuterated alkanes has been found only in the case of propane; with methane and ethane, only stepwise exchange was observed. In early studies it was found that the ratio of mono to perdeutero compounds was nearly independent of temperature and

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conversion and depended only on the temperature of activation. However, a greater proportion of multiple exchange was later reported (1) on chromia gel, probably due to a slight change in the activation procedure. For instance, in cyclopentane, a 1:2 ratio of multiple to stepwise exchange was observed, which is much larger than was reported earlier (1:16) (*7*). The same is true for *n*-hexane exchange where a 1:38 ratio was changed to 1:5.6. These changes were probably due to the transformation of the gel to a microcrystalline form, initiated, for example, by long use of the catalyst.

Burwell *et al.* (*1, 3, 4*) originally explained the mechanism of alkane deuterium exchange by considering it as a reverse reaction of olefin hydrogenation. Based on the deuterium distribution, they found that migration of deuterium atoms on the surface occurs much faster than the deuteration of ethylene. Later, Burwell *et al.* themselves questioned the existence of the same mechanism for olefin hydrogenation and alkane exchange, although the half-hydrogenated forms were assumed to operate in both cases (*1*). However, the temperature range is completely different; therefore, one cannot assume the same interaction between the hydrocarbon and the active sites.

As already mentioned, perdeuterated compounds were formed on chromia gel only after long use. One may postulate that multiple exchange is a specific feature of crystalline α-chromia formed in a thin layer on the gel surface during long treatment. To resolve this we have studied, in the present work, the deuterium exchange of hydrocarbons on α-chromia of well-defined structure and have compared it to the results obtained on chromia gel.

In addition to a detailed kinetic investigation of the exchange reactions of methane, ethane, and propane on α-chromia, which has never been made before, we have also carried out experiments to find out the parameters (e.g., effect of oxygen and decay of catalytic activity due to hydrocarbon species) by which the selectivity of multiple/single exchange is influenced. The studies have been supplemented by the results of other physical methods, e.g., IR spectroscopy.

EXPERIMENTAL

Apparatus. An all-glass circulation type reactor was used and connected to an AEI MS 10 C2 mass spectrometer through a capillary leak. Details of the apparatus have been given elsewhere (*8*). With this equipment the progress of exchange can be continuously monitored. The experimental data were obtained after applying the necessary corrections for naturally occurring ^{13}C and for fragmentation. The rate of exchange was evaluated by the formation of deuterated species and/or by the consumption of light hydrocarbons (*9*).

Catalyst. α-Chromia was prepared by thermal decomposition of $(NH_4)_2Cr_2O_7$, followed by treatment of the powder formed with air at 953°K. The product was a fine green powder which contained only α-chromium(III) oxide, as based on X-ray diffraction results. The line at 0.255 nm characteristic of chromium(VI) oxide (*10*) was missing.

Further studies also showed that the catalyst formed in this way was a uniform substance. In a DTA measurement, no peak appeared to around 723°K; such a peak is characteristic of the transformation of the gel structure into the microcrystalline form (*11*).

Chromia gel obtained from Professor R. L. Burwell, Jr. was also used as a catalyst for comparison. This was activated as described earlier (*4*).

The surface area of the α-chromia, measured by the BET method using nitrogen, was 18.2 $m^2\ g^{-1}$. For this experiment, a catalyst diameter between 0.1 and 0.3 mm was used.

Reagents. Hydrogen and deuterium gas were purified by passage through a deoxo unit and by diffusion through a heated palladium thimble. Hydrocarbons (analytical grade, supplied by Fluka) were further purified by triple distillation at liquid nitrogen temperature. CD_4 and C_2D_6 (produced by Isocommers, Berlin) underwent the same procedure. Infrared spectra of the fresh and treated (see later) α-chromia samples were obtained with a Perkin–Elmer Type 325 spectrometer. The catalyst samples were mixed with KBr in a ratio of 3:100 after treatment. During the treatment with deuterium and oxygen, the water formed was trapped using liquid nitrogen.

RESULTS

1. Stable Activity of Catalyst

The fresh catalyst was activated in a hydrogen atmosphere (10.1 kN m^{-2}) for 48 h and the rate of exchange was determined by using a 10:1 deuterium–methane mixture at 646°K (the amount of methane was 8×10^{-5} mol). After this reaction, α-chromia was regenerated by circulating deuterium gas overnight at 743°K. After this treatment, the catalytic activity as characterized by the rate of exchange was not completely restored due to the fact that the hydrocarbon residue was not removed by deuterium. (In the circulating deuterium, approximately 10^{-7} mol of methane was recovered, and an additional amount was removed after oxygen treatment.)

Beside the decay in catalytic activity due to hydrocarbon residues, there is another factor which decreases the catalytic activity, namely, if the initial hydrogen treatment is carried out for longer than 48 h a smaller catalytic activity is observed compared to that obtained after 48 h treatment.

After several experiments, it was found that treatment of the fresh catalyst with hydrogen or deuterium for 168 h produces a stable activity level which is about 30–40% of the original value. Further activity decreases of α-chromia can be neglected in the subsequent reactions if the following procedure for regeneration is applied: evacuation of the catalyst to 1.33×10^{-6} kN m^{-2} after each run, followed by overnight treatment with deuterium (6.65 kN m^{-2}) at 748°K and evaluation to 1.33×10^{-6} kN m^{-2} simultaneously cooling down to the temperature of the next run.

The activity of the catalyst is extremely sensitive to oxygen. By exposure of the catalyst to air, even for a short period of time at room temperature (which first happened accidentally), the activity was increased by several orders of magnitude, and the previously mentioned long hydrogen treatment was necessary to achieve a stable activity level appropriate for kinetic measurements.

When the oxygen effect was studied, the following procedure was applied: After reaction, the catalyst was purged with deuterium followed by evacuation to 1.33×10^{-6} kN m^{-2} of pressure, and then oxygen at a pressure of 39.9 kN m^{-2} was admitted into the system. After an hour, the catalyst was evacuated, and the ethane–deuterium exchange was commenced as a test run.

2. Kinetics of Deuterium Exchange in Methane, Ethane, and Propane

Deuterium exchange in methane, ethane, and propane commences at considerably higher temperature than in the case of metal catalysts (*12, 13*). Kinetic measurements were carried out in the temperature ranges of 579–688, 569–682, and 550–646°K for methane, ethane, and propane, respectively. The rate of exchange was characterized either by k_ϕ as given by Kemball (*14*) or by the initial rate of the disappearance of light hydrocarbons (w_{d_0}).

Activation energies and pre-exponential factors are summarized in Table 1. Two characteristic behaviors emerge from the

TABLE 1

Kinetic Parameters of Exchange Reaction of Methane, Ethane, and Propane

Substance	D_2/HC	E (kJ mol^{-1})	log A (molecule sec^{-1} m^{-2})	r/r_{CH_4}[a]	r/r_{CH_4}[b]
Methane	10:1	88.6[c]	—	1	1
	10:1	96.1[d]	23.42		
	4:1	98.0[d]	23.76		
Ethane	10:1	127.0[c]	—	1.5	1
	10:1	137.0[d]	26.93		
	10:1	132.5[e]	28.90		
Propane	10:1	85.3[c]	—		
	10:1	84.4[d]	23.28	6.7	3.4
	7:1	97.4[d]	24.45		

[a] Measured at $T = 646°K$ using initial rate of light hydrocarbon disappearance.

[b] Measured at $T = 646°K$ using initial rate per hydrogen substitution.

[c] Determined by k_ϕ.

[d] Determined by w_{d_0} as the number of moles of light hydrocarbons which disappeared per minute initially.

[e] Determined by w_{d_0} after exposure of the catalyst to air.

data of Table 1. First, above 611°K, the rate of exchange increases with carbon number in the hydrocarbons. This result does not contradict those given by Burwell *et al.* on chromia gel catalyst (*4*), because their measurements were carried out below 611°K in which range the relative rates of methane and ethane are reversed due to the difference in activation energy. Second, the activation energy for ethane is about 41.8 kJ mol^{-1} higher than the values for methane and propane. The pre-exponential factor for ethane is also higher. Similar results were obtained by Burwell *et al.* on chromia gel (*4*). The absolute values on gel are a little different from those measured on α-chromia, but this is probably due to the different conditions of the surface of the two types of catalysts.

The activation energies measured at different deuterium–hydrocarbon ratios are the same, but we can observe a slight tendency of the pre-exponential factor to increase, showing that, by increasing the hydrogen pressure, only the number of active sites is decreased.

As mentioned earlier, an enhancement of catalytic activity occurred by exposure to air. In Table 1, the fifth and sixth rows show that there is no change in the energy of activation, but again the pre-exponential factor increases.

Since the catalytic exchange reaction apparently follows first-order kinetics on isotope composition, experiments were carried out to measure the actual order of reaction with respect to hydrocarbons and deuterium. The data are summarized in Table 2.

The apparent orders of reaction with respect to hydrocarbons are independent of temperature in the case of methane and propane. The order of reaction with respect to deuterium is slightly negative and tends to decrease with increasing carbon number One of the main characteristics of the reaction order results is that the deuterium order is less negative compared to those obtained on metals (*13*, *14*), while the hydrocarbon order is nearly the same in both cases. For instance, deuterium orders on nickel for methane, ethane, and propane are −1, −0.8, and −0.7, respectively.

The isotope effect of exchange was measured in order to obtain information about the nature of the rate-determining step.

Mixtures of light alkane and deuterium gas as well as perdeuterated hydrocarbons and hydrogen gas were reacted on the same α-chromia catalyst; k_ϕ^H as well as k_ϕ^D were measured. The following mixtures were used: CH_4 (1.2×10^{-4} mol) + D_2 (7.8×10^{-4} mol) and CD_4 (1.2×10^{-4} mol) + H_2(7.8×10^{-4} mol) at a temperature range of 593–653°K; C_2H_6 (7.1×10^{-5} mol) + D_2 (6.5×10^{-4} mol) and C_2D_6 (7.1×10^{-5} mol) + H_2 (6.5×10^{-4} mol) at a temperature range of 593–653°K. At low temperature, the k_ϕ^H/k_ϕ^D ratio had a value between 1.5 and 2. At the upper limit of the temperature range, this ratio decreased to a value of 1. Thus, the kinetic isotope effect due to the higher reactivity of the C–H bond disappears at high temperature.

3. *Distribution of Deuterated Species*

All experiments were carried out at the same temperature using a 10:1 deuterium–hydrocarbon mixture. The rate of exchange was characterized by the initial rate of disappearance of the light hydrocarbon. The percentage distributions of deuterated species are summarized in Table 3.

The main feature of the deuterium distribution is that it does not follow stepwise exchange, as is shown by comparison of the experimental data with those calculated on the basis of a binomial expansion. Regardless of the catalytic activity and conversion, the formation of perdeuterated species can be observed in all cases.

From the point of view of maxima in the distribution, methane and propane can be handled as one type of exchange. It is clear from Table 3 that, in most cases, maxima can be observed only for monodeuterated and perdeuterated species. The regularity for the relative proportion of these species is that, on a more active catalyst, perdeuterated species are formed in greater amounts, whereas at higher conversion, regardless of the activity level, the relative proportion of monodeuterated species increases.

On the other hand, ethane behaves differently from the other two hydrocarbons. Maxima can be observed at ethane-d_2 and, to a small extent at other species containing even numbers of deuterium atoms.

4. *Effect of Surface Modification on Deuterium Distribution*

(*i*) *Effect of self-poisoning.* Experiments were carried out to elucidate why the ratios of these maxima can be changed at different activity levels and at different conversions. Based upon the disappearance of light hydrocarbons, the rate of exchange is constant, and it is not diminished by the progress of reaction.

However, at higher conversion, the proportion of the monodeuterated species increases as compared to the perdeuterated

TABLE 2

Order of Exchange Reactions with Respect to Hydrocarbon and Hydrogen

Order of reaction	Methane	Ethane	Propane
With respect to deuterium	0.0 (598°K)	−0.3 (598°K)	−0.2 (556°K)
	−0.1 (651°K)	−0.3 (646°K)	−0.3 (588°K)
	−0.2 (682°K)	−0.4 (682°K)	−0.8 (646°K)
With respect to hydrocarbons	0.9 (614°K)	0.7 (601°K)	1.2 (558°K)
	1.0 (656°K)	0.9 (646°K)	1.2 (588°K)
	0.9 (688°K)	1.0 (682°K)	1.2 (646°K)

TABLE 3

Percentage Distribution of Deuterated Species under Different Conditions

Hydrocarbon	$w_{d_0} \times 10^{-10}$ mol sec^{-1} m^{-2}	Conversion[a]	Percentage distribution of deuterated species							
			d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Methane	1.1	0.18	16.7	5.5	11.1	66.7				
	4.0	0.30	10.5	7.0	8.8	73.7				
	—	—	(100.0)	(0)	(0)	(0)				
	1.1	2.25	88.5	1.8	0.8	8.8				
	4.0	2.02	87.5	2.0	1.0	9.4				
	—	—	(99.0)	(1.0)	(0)	(0)				
Ethane	2.8	2.51	18.6	33.7	0.8	13.4	7.9	25.4		
	138.0	4.47	2.4	89.5	1.1	4.0	0.4	2.5		
	—	—	(98.8)	(1.2)	(0)	(0)	(0)	(0)		
	1.4	12.78	81.3	11.1	0.8	2.5	1.5	2.8		
	—	—	(94.3)	(5.4)	(0.1)	(0)	(0)	(0)		
	114.0	10.70	8.6	51.7	3.9	8.0	11.1	16.6		
	—	—	(95.3)	(4.6)	(0.1)	(0)	(0)	(0)		
Propane	7.8	1.45	68.0	1.0	1.0	1.5	2.0	1.0	6.1	19.3
	12.0	1.80	16.0	2.6	1.0	3.6	1.0	1.0	21.4	53.5
	—	—	(99.3)	(0.7)	(0)	(0)	(0)	(0)	(0)	(0)
	5.3	11.60	85.4	8.7	0.1	0.5	0.2	0.1	0.8	4.0
	—	—	(94.6)	(5.2)	(0.2)	(0)	(0)	(0)	(0)	(0)
	11.0	10.11	38.1	0.1	0.1	0.1	0.1	0.1	20.0	41.3
	—	—	(94.5)	(5.4)	(0.1)	(0)	(0)	(0)	(0)	(0)

[a] $T = 646°K$; conversion is calculated as $100 \times (1 - d_0/100)$, where d_0 is the percentage amount of the light hydrocarbons. Values in parentheses are the distributions calculated by binomial expansions.

one. This is probably due to a successive blocking of the sites which are responsible for the formation of perdeuterated species. Here we assume that this blocking is caused by the hydrocarbons which have already visited the surface; therefore, the more hydrocarbon molecules that strike the surface the more sites that are blocked.

Temperature can affect this blocking in the same way. At higher temperature, the exchange takes place faster, and, therefore, at the same initial time interval (after the beginning of reaction), the conversion is higher. This means that at a higher temperature more hydrocarbon molecules attack the surface, and, as a result, one can observe a distribution different from that obtained at low temperature. This is demonstrated in Fig. 1.

Further indication of this "self-poisoning" effect can be obtained from a plot of the methane-d_4/methane-d_1 ratio as a function of time at different temperatures (Fig. 2).

The poisoning effect, however, is reversible, because, after the regeneration proccess at the end of a run, active sites can be restored. Thus, self-poisoning is likely to be due to the hydrocarbon residues which are strongly, but not irreversibly, chemisorbed on a part of the surface where they remain as long as the reaction takes place.

(*ii*) *Effect of oxygen.* We have already reported an increase in catalytic activity of α-chromia treated in hydrogen and exposed to air afterward. It is interesting to show data on an exchange reaction carried out on a catalyst exposed to oxygen. In Fig. 3, exchange between ethane and deuterium is presented on the catalyst normally used and on the same catalyst exposed to

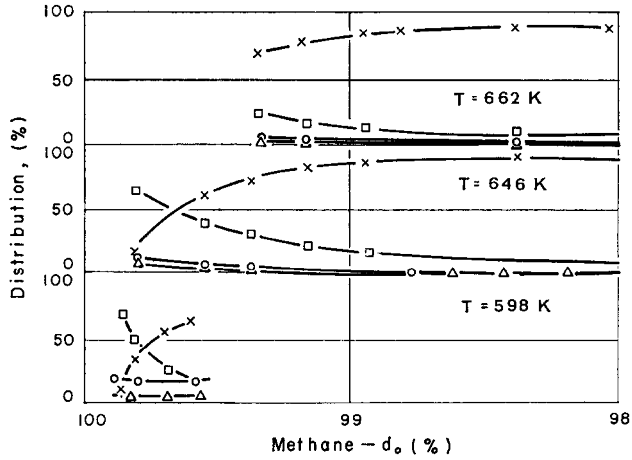

FIG. 1. Distribution of deuterated species in methane exchange at different temperatures. Symbols: (**X**) methane-d_1, (○) methane-d_2, (△) methane-d_3, (□) methane-d_4.

oxygen. The catalyst treated with oxygen before the run behaves like the hydrogen-treated chromia, but, after a short period of time, the reaction starts to accelerate, and, after 10 min, the consumption of light ethane is stabilized at a higher rate. No change in temperature dependence emerges, as seen in Fig. 4, but the rate of exchange increases several times. However, it seems that the relative amount of ethane-d_2 and perdeuterated ethane is greater on α-chromia treated by oxygen than on the original (see Table 4). In order to elucidate the effect of different treatments on the surface of chromia IR, spectroscopy was used.

Figure 5 shows that spectra of a fresh sample (A) and one which was exposed to

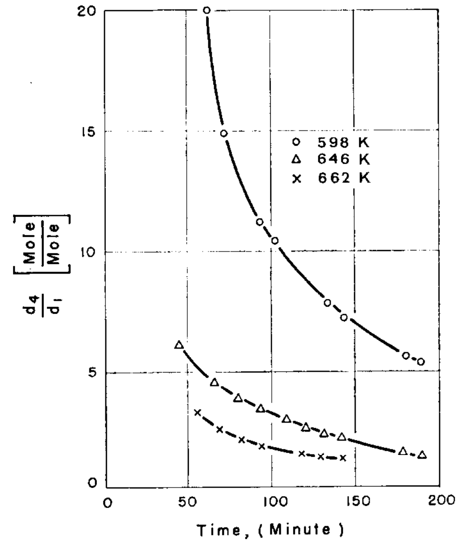

FIG. 2. The change of methane-d_4/methane-d_1 ratio as a function of reaction time at different temperatures.

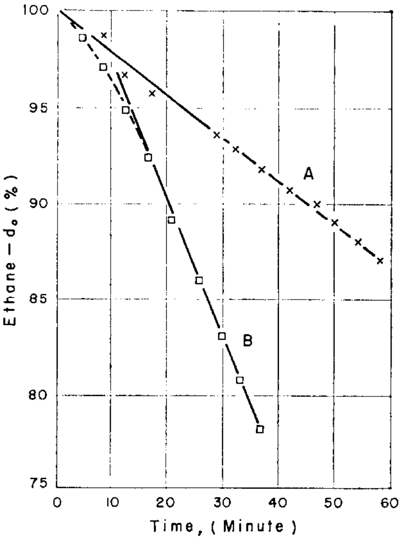

FIG. 3. The consumption of light ethane as a function of time: (A) hydrogen-activated α-chromia; (B) oxidized α-chromia.

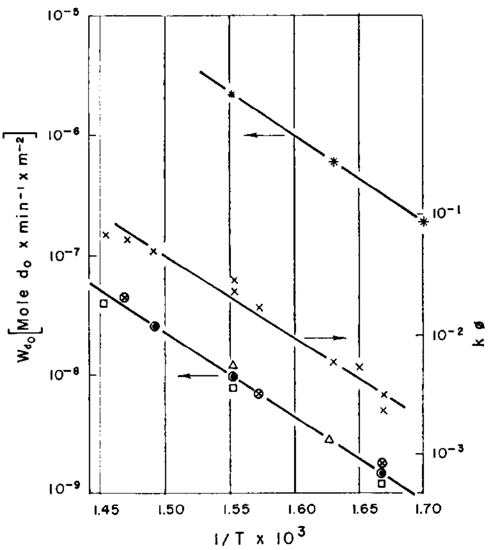

FIG. 4. Arrhenius plots of the initial rates and k_ϕ of ethane exchange. Symbols:

	C_2H_6 (moles)	D_2 (moles)
⊗	7.5×10^{-5}	9.1×10^{-4}
□	7.4×10^{-5}	8.7×10^{-4}
⊙	8.4×10^{-5}	8.9×10^{-4}
△	1.4×10^{-4}	1.3×10^{-3}
*	After oxygen exposure at room temperature.	
×	k_ϕ from all experiments.	

oxygen for 3 h at 743°K after hydrogen treatment (B) are very much like each other.

The minor peaks between 936 and 840 cm^{-1} probably correspond to different types of surface oxygen compounds. If these two spectra are compared to those obtained after treatment with hydrogen at 743°K for 12 h (C) and after interaction with methane for 2 h at 673°K (D), the main difference appears in that region. Here, the spectra are simplified due to the reduction of the catalyst surface and the disappearance of a part of the oxygen.

(*iii*) *Comparison of α-chromia with chromia gel.* In Fig. 6, the percentage distribution of deuterated isomers (neglecting d_0) is compared for the case of chromia gel and α-chromia catalysts. The data obtained at 618°K clearly show that the rate of change with conversion of the relative amount of ethane-d_1 to ethane-d_2 is similar in both cases, but the absolute value of ethane-d_2 is higher on α-chromia. At higher conversion, the distribution on chromia gel becomes very close to the statistical one.

DISCUSSION

1. *Nature of Active Sites*

Many controversial data have been published about the nature of active sites on the chromia catalyst. Since the catalyst used in the present work was pretreated at a high temperature in oxygen atmosphere, it is reasonable to assume the existence of chromium ions in a valence state higher than 3+ as active sites. Indeed, according to Andreev *et al.* (*15*, *16*), Cr_2O_3 calcined in air at 1073°K contains 0.16 mg of Cr^{6+} ions/g of catalyst on the surface. Surface oxidation has also been proposed by other authors (*17*, *18*), and chromium ions of valence states higher than 3+ were considered to be responsible for some hydrocarbon reactions (*19*). ESR measurements have shown that these active sites can be removed by reduction only at high tem-

TABLE 4

Effect of Treatment on Deuterium Distribution in Ethane[a]

Conversion exchange (%)	Percentage of deuterated species						Remarks
	d_1	d_2	d_3	d_4	d_5	d_6	
80.2	9.9	41.6	5.4	9.2	17.2	16.2	Oxygen-treated
81.1	80.5	13.3	1.0	2.6	0.6	0.7	Hydrogenated

[a] $T = 646°K$; $n_{C_2H_6} = 7.14 \times 10^{-5}$ mol; $n_{D_2} = 6.33 \times 10^{-4}$ mol.

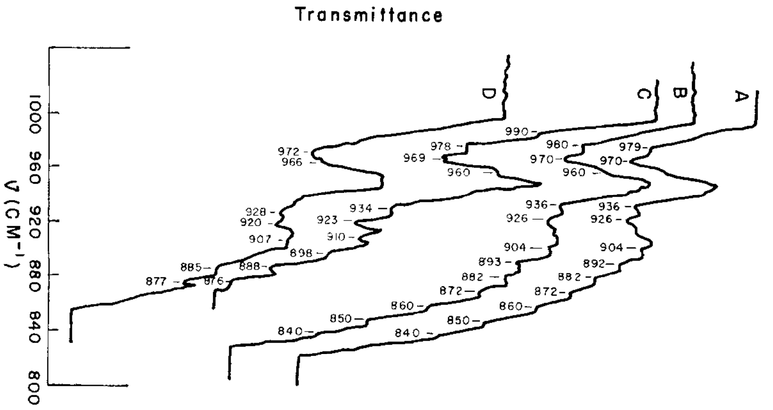

FIG. 5. IR spectra of different treatments of α-chromia catalyst: (A) fresh samples; (B) treated in oxygen; (C) treated in H_2; (D) treated in methane.

perature, whereas calcination of the same sample at 823°K is not the appropriate condition to restore the Cr^{6+} ions on the surface.

In contrast to the work of Andreev *et al.* (*15, 16*), Selwood (*20*), McIver and Tobin (*21*) and Weller and Voltz (*22*) claimed that reductive treatment with hydrogen may produce surface chromium ions in an oxidation state lower than 3+. According to Selwood (*20*), a high-temperature oxygen treatment followed by reduction at 548°K was found to be a method for activation of α-chromia. Hydrogen treatment above this temperature slowly destroys the sites proven to be active in the H_2–D_2 exchange reaction (which can be considered as a measure of activation of hydrogen).

Since, in our case, Cr_2O_3 was pretreated in oxygen followed by activation in hydrogen, we are inclined to consider the Cr^{3+} ions sitting in octahedral positions on the surface as active sites. The following arguments may be advanced to support this idea.

(i) The rate of exchange per unit surface area is much higher on gel activated by helium treatment (*4*) than on α-chomia activated by long hydrogen treatment. This difference is probably due to the drop in the number of surface Cr^{3+} ions under the effect of hydrogen. Another possibility might also be the operating, namely, the partial filling up of active sites with hydrogen as has already been suggested (*20*).

(ii) The effect of oxygen also supports this picture. Although Cr^{3+} can be reduced to Cr^{2+} with great difficulty (a conversion of octahedral to tetrahedral position of chromium ion), the occurrence of this process on the surface itself cannot be omitted. Since surface Cr^{2+} ions in tetrahedral coordination are unstable, they can be easily oxidized again into stable Cr^{3+} ions by using even mild oxygen treatment. The depletion of oxygen on the surface layer of chromia under the effect of a

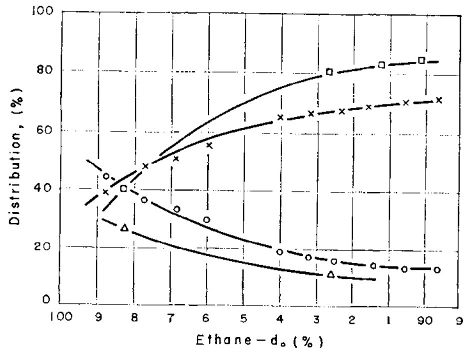

FIG. 6. Comparison of ethane-d_1 and ethane-d_2 formation as a function of conversion chromia and on α-chromia. Symbols: on α-chromia: (X) ethane-d_1, (O) ethane-d_2; on chromia gel: (□) ethane-d_1, (△) ethane-d_2.

reducing atmosphere such as hydrogen and hydrocarbon can be detected by IR spectroscopy (see Fig. 5).

2. Kinetics of Exchange

In comparison to gel, the deuterium exchange properties of α-chromia are very similar in regards to the energy of activation, but the rate of exchange on chromia gel is higher than it is on α-chromia (*4*).

On the other hand, α-chromia is remarkably different from transition (or VIII b) metals in many respects. Thus, the temperature of exchange is higher by about 100°K, and the rate of exchange is one or two orders of magnitude lower on chromia than on these metals. The most remarkable difference is shown in the distribution of deuterated species. On chromia, the main product is the monodeuterated hydrocarbon, whereas, on metal (e.g., nickel), this species is completely missing sometimes (*12*).

Besides temperature range and rate of exchange, there are two main ways in which α-chromia differs from VIII b metals. One of these is in the order of reaction with respect to deuterium, which is less negative than in the case of metals. Hydrogen adsorption cannot, therefore, be considered as a process which occurs to a much larger extent than that of hydrocarbons. This is well-supported by the fact that H_2–D_2 exchange takes place at low temperatures on metals, whereas, on α-chromia, it shows a high rate only above 473°K (*20*). A less favorable adsorption of deuterium is, therefore, the reason for the less negative order in the exchange reaction as compared to metals. In addition, the deuterium order becomes more negative as we proceed from methane to propane, and this is opposite to what is found on metals.

The other characteristic feature of the exchange reaction is the energy of activation, which passes through a maximum in the sequence of methane–ethane–propane. Since we have found an isotope effect with respect to the rupture of the C–H and C–D bonds in hydrocarbons, the C–H bond splitting can be considered as the rate-determining step. If a covalent bond had formed between the catalyst and hydrocarbon during the exchange reaction, a decreasing trend in activation energy should have been obtained, as we have found for metals. On chromia, the trend of activation energies is opposite to what we would expect on the basis of C–H bond strength, and, therefore, the hydrocarbon intermediate may not be attached to Cr^{3+} ions by a covalent bond. Cr^{3+} ions sitting in an octahedral position are surrounded by oxygen ions, and these can be used for attaching charged species. Thus, for instance, H^+ from methane can be accommodated on one of the oxygen ions and CH_3^- itself can bond to chromium ions. Because of the mobility of H and deuterium ions at the temperature of exchange, one of the deuterium ions can be picked up by the hydrocarbon, and the latter can desorb as a deuterated product. In the case of ethane, due to the additional methyl group, the formation of the carbanion is hindered, and, therefore, the activation energy is higher.

In the case of propane, the energy of activation is lower, again probably due to the presence of a $-CH_2-$ group in the molecule. We may explain this by the existence of a different mechanism which is probably the formation of π-allyl species as proposed in the case of butane isomerization (*23*). This is reflected also in the initial rate of exchange referring to one hydrogen atom (Table 1, last column). This value is much larger than the corresponding ones for methane and ethane, because π-allyl formation facilitates the exchange of all hydrogen atoms in propane.

By adopting this view, the effect of oxygen can be understood. The energy of activation of exchange is unchanged by the effect of oxygen; therefore, only the number of sites is increased, by converting

Cr^{2+} into Cr^{3+} ions on the surface. The formation of excess oxygen reported by McDaniel and Burwell (*24*), as possibly the formation of Cr^{5+} from Cr^{3+} on the surface of crystalline Cr_2O_3 (*25, 26*), may be of secondary importance, because it refers to a highly dehydroxylated surface. The anomaly, however, that we found for the initial rate of exchange on oxygen-treated catalyst may be due to this effect, namely, the smaller initial rate in Fig. 3 is due to the fact that, first, Cr^{2+} is partly oxidized into Cr^{5+} and Cr^{6+} by oxygen, and then these ions are successively reduced to active Cr^{3+} under the effect of the reaction mixture.

Since crystalline chromia is thermodynamically more stable than gel, the coordinatively unsaturated Cr^{3+} ions are probably bonded more strongly to the bulk. Consequently, the Cr–X bond (H, C) will be weaker. Therefore, the reaction requires higher activation energy, and, this, in fact, is reflected in the difference in the absolute values of the activation energies between α-chromia and chromia gel.

3. *Mechanism of Exchange Reactions*

We believe that the existence of dual Cr^{3+}–Cr^{3+} sites on α-chromia is the main reason for observing multiple exchange. Tétényi *et al.* have proven the importance of the magnitude of the valence angle of C–C–M in the case of ethane exchange on Ni and Pt, where the values are 103.4 and 106.4°, respectively (*27*). If the structure of α-chromia is considered, several Cr^{3+}–Cr^{3+} pairs can be found, e.g., on the (210) surface at a distance of 0.265 and 0.289 nm, calculated by Dyne *et al.* (*28*) which are appropriate for the formation of diadsorbed ethane. The C–C–Cr valence angles on the formation of 1,2-diadsorbed ethane are 105.3 and 107.7° which are very close to the values found for metals.

If the number of these sites is increased, α-chromia becomes more active in multiple exchange, and, consequently, the selectivity for multiple/single exchange is increased. Conversely, the opposite effect can be observed if these sites are partially blocked by any source (such as hydrocarbons) or are diminished by hydrogen treatment. This explanation is supported by the fact that the relative proportion of ethane-d_2 isomers is enhanced after oxygen treatment, because the large number of Cr^{3+}–Cr^{3+} pairs formed is a reason for the privilege of 1,2-interaction.

The existence of 1,2-adsorption may be a reasonable explanation for the formation of perdeuterated species in the case of ethane. However, the high amount of perdeuterated methane cannot be ascribed to this mechanism. Here we have to assume the formation of $Cr{=}CH_2$ and, in this way, the large amount of CD_4 is completely understandable. This idea is well-supported by a number of analogous carbene-type complexes in the homogeneous phase (*27*).

The rate of exchange per hydrogen atom for propane is about six times faster than those for methane and ethane. In addition, with a diminishing number of dual sites (at higher conversion), the proportion of perdeuterated propane is still high. This is because the exchange does not occur mainly via 1,2-diadsorbed species as in the case of ethane, but via the π-allyl species. This supports very well the mechanism that was found by Haller and Saint-Jost (*23*) and explains why the energy of activation decreases again as compared to ethane.

The mechanism of exchange can be further clarified by comparing our results with those of ethane dehydrogenation producing ethylene on the same catalyst. At 646°K a small amount of ethylene is formed (*30*). The energy of activation of ethylene dehydrogenation is very similar to that of the exchange of ethane (146.7 kJ mol^{-1}). This resemblance strongly supports the importance of 1,2-diadsorbed species in both alkane exchange and ethane dehydrogenation. This is opposite to what was found in olefin hydrogenation (half-hydrogenated form).

The existence of 1,2-diadsorbed species in the case of ethane is supported by the high value of the activation energy as compared to methane and ethane. The formation of this species is not as easy as on metals because the surface Cr^{3+} ions are surrounded by O^{2-} and OH^- ions which make the two chromium ions less accessible to the reactant.

In our experiments on gel, multiple exchange was also observed, and this is opposite to what Burwell *et al.* found (*4*). In our opinion, this difference can be ascribed to the fact that, in earlier experiments, the distribution of the deuterated species was measured at higher conversion. Since our work displayed a conversion dependence of the relative amount of deuterated species due to the strong chemisorption of hydrocarbon residues on the dual sites, one can expect a statistical distribution at higher conversion to a larger extent.

In comparing the behavior of α-chromia and chromia gel (*4*), the main difference is in the enhanced rate of formation of perdeuterated species on α-chromia. For this, the different geometry of sites on the two catalysts may provide an explanation. On gel, isolated chromium sites are responsible for the exchange, whereas, on α-chromia, pair sites (dual sites) can be found due to the high degree of dehydroxylation (*1*). As already mentioned, Burwell *et al.* already found a decrease in the ratio of mono to perdeutero compounds depending on the prehistory of the catalyst. Even on the same catalyst after long use a decrease in the aforementioned ratio was observed. This means that, due to the higher population of the Cr^{3+} ions on the surface, the multiple exchange is more important on α-chromia. The trends shown in the activation energies are the same, but the absolute values are less on gel compared to those on α-chromia.

Now, the explanation for the difference between the behavior of chromia and metals is not too difficult. Since metal atoms in α-chromia are surrounded by inert oxygen ions, which may not be centers for hydrocarbon adsorption, the surface concentration of metal sites is much less on chromia than that on a metal. Even if metal ion pairs are available, they are not in the conformation which can easily accommodate a 1,2-diadsorbed radical on the surface. On the other hand, Cr^{3+} ions are surrounded by negatively charged OH^- and OD^- ions; therefore, hydrogen atoms may not be formed on the surface, and, thus, the formation of covalent bonds between deuterium and Cr^{3+} is not important. The same is valid for the $C–Cr^{3+}$ bond, and, consequently, this may not play a role in the exchange reactions.

CONCLUSIONS

It has been established that hydrogen–deuterium exchange between simple saturated hydrocarbons and deuterium gas takes place on α-chromia in a way similar to that found on chromia gel. The main difference between these two catalysts exists in the geometric arrangement of the two surfaces as well as in the bond strength of surface chromium ions to the bulk.

The behavior or α-chromia can be explained in exchange reactions by the formation of polarized C–Cr and H–O bonds on the surface which are responsible for the single exchange. The existence of dual sites promotes the multiple exchange of deuterium atoms in hydrocarbons.

Multiple exchange also takes place on chromia gel but this is strongly affected by long use of the catalyst. The anomaly found in the literature for gel catalyst can be interpreted by the conversion dependence of multiple exchange.

The effect of hydrogen as well as oxygen points to the fact that only one type of ion, viz. Cr^{3+}, is responsible for the catalytic activity.

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