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Activity and Mechanism of the Catalytic Action of Rare-Earth Oxides in Low-Temperature Ethylene Hydrogenation

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The variation in catalytic activity of rare-earth oxides and their analogs, scandia and yttria, in ethylene hydrogenation between −120 and 20°C has been studied as a function of the temperature of pretreatment. Thermal analysis has been used to study the decomposition of the hydroxides from which the oxides were prepared. The oxides show catalytic activity after pretreatment at 600°C when dehydration, decarboxylation, and denitroxylation have gone to completion and, in addition, when partial dehydroxylation of the surface has also taken place. Sesquioxides showed high activity, whereas dioxides were of low activity. A decrease in hydrogenating activity in the series of oxides from lanthana to lutecia correlates with a decrease in their basicity. As was shown by means of thermodesorption, hydrogen and ethylene are chemisorbed in two forms. With dysprosia, it has been shown, by using deuterated species, that ethylene hydrogenation proceeds by involving loosely bound forms of hydrogen and ethylene via a semihydrogenated complex. Associatively adsorbed ethylene is involved in the reaction, and hydrogen activation is likely to be the limiting step.

INTRODUCTION

A theory to predict the catalytic activity of oxide systems in hydrogenation reactions cannot be developed without elucidating certain regularities in the variation of the catalytic activity of different elements in the Periodic Table. Of particular interest is the investigation of oxides of transition elements, the properties of which vary as their inner orbitals are filled with electrons. Such as examination has been carried out only for the first row of transition metal oxides (*1*). As correctly shown by Germain (*2*), however, it is necessary to consider the pretreatment of the oxide, and this fact lends doubt to the significance of finding regularities. The difficulty of comparing oxides in high-temperature catalysis is made worse by interaction of the oxides with the reacting substances.

By measuring the activities for the low-temperature hydrogenation of ethylene for the entire lanthanum series of rare-earth oxides it is possible to estimate the role of pretreatment on the catalyst. In the course of this investigation, we will propose that a comparison of the maximum specific activities of the oxides reveals a connection between catalytic activity and basicity of the oxide. For comparison, the catalytic activities of scandium, yttrium, zirconium, hafnium, and chromium oxides have also been studied.

EXPERIMENTAL

The oxide catalysts were prepared by thermal decomposition of hydroxides. The latter were precipitated from nitrate solutions with 10% ammonia at pH 8–9, washed with distilled water to remove

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NO_3^--ions, dried at 110°C for 2–3 h, and then pressed into pellets. The purity of the oxides was 99.7%. A commercial neodymia (Nd_2O_3*) (RZTU N 1076-63 H-2) was also used as a catalyst, as was chromia, which was obtained by decomposition of chromium anhydride *in vacuo* at 500°C, followed by reduction with hydrogen at the same temperature. The samples were heated to a predetermined temperature *in vacuo*, at a rate of 2°C/min, *in situ* in the reaction vessel used to measure catalytic activity. The specific surface of the oxides was measured by low-temperature nitrogen adsorption (*3*). The relative error of the measurements did not exceed ±5%.

Differential thermal and thermovolumetric analyses (DTA and DTVA) in a stream of nitrogen, helium, and hydrogen were used to study the processes occurring upon hydroxide decomposition. The experiments were carried out (*4*) over the temperature range 20–1000°C with uniform heating at a rate of 20°C/min.

The activity of the catalysts was studied in a glass circulating system (*5*) with a volume of 0.6 liter. The weight of the sample was about 3.5 g. Before each experiment, the samples were evacuated at 10^{-5} Torr at a predetermined temperature. Ethylene hydrogenation was performed in the temperature range −120–20°C, with an initial pressure of about 10 Torr for the reaction mixture and a reactant ratio of $H_2/C_2H_4 = 1.2$. The reaction was followed by recording the variation in the total pressure of the mixture and by noting the hydrogen partial pressure upon freezing out of the hydrocarbons with liquid nitrogen. Mass-spectrometric and chromatographic analyses were performed which demonstrated that, in each case, the hydrogenation proceeded selectively without formation of side products. Mass spectrometry was also used in the experiments with isotopic species (D_2 and C_2D_4) (*5*). The activity of the oxides was estimated from the specific rate of ethylene hydrogenation at 50% conversion, as determined from the slope of the tangents drawn to the curve of conversion versus time. The error in measuring the specific rate did not exceed ±20%.

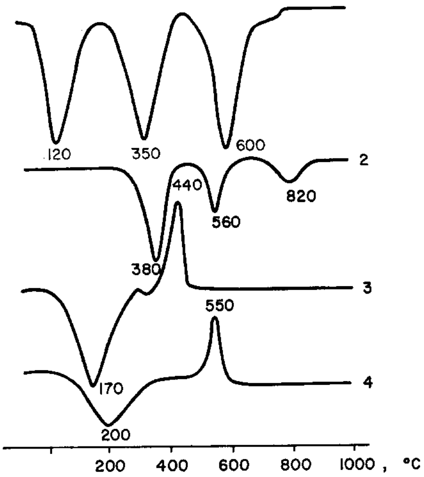


FIG. 1. Curves of DTA in nitrogen. (1) $Nd(OH)_3$; (2) commercial Nd_2O_3; (3) $Zr(OH)_4$; (4) $Hf(OH)_4$.

Hydrogen, ethylene, ethane, nitrogen and helium were purified by successive passages through columns of preheated γ-Al_2O_3, reduced Ni–Cr catalyst, and potassium hydroxide. In addition, hydrogen and helium were passed through a trap cooled in liquid nitrogen, whereas ethane and ethylene were subjected to low-temperature distillation. When the reaction mechanism was studied, hydrogen and deuterium were purified by diffusing them through palladium. The content of the prevailing isotope in deuterium was 99%. Deuteroethylene contained 99% of the dominant substance-($C_2D_4 + C_2D_2H_2$) and 97% C_2D_4.

Thermodesorption measurements were performed in the temperature range from −78 to 800°C. Before adsorption, the oxides were heated *in vacuo* at temperatures at which they exhibited their highest catalytic activities. The gases were adsorbed at −78, −55, 20°C. Then, the samples were evacuated at 10^{-3} or 10^{-5} Torr and were

TABLE 1

The Effect of Vacuum Treatment Temperature on Oxide Activity

Temperature (°C)		Ethylene hydrogenation rate ($r \cdot 10^9$ mole/m^2·sec)											
Treatment *in vacuo*	Experiment	Nd[a]	Sm	Eu	Gd	Dy	Ho	Er	Tu	Yb	Lu	Sc	Y
700	−55	0.35	0.75	0.5	0.65	0.2	0.35	0.45	0.3	—	0.3	0.1	0.75
800	−40	3.8	3.05	2.1	3.25	1.1	1.25	1.1	1.1	—	1.3	0.75	—
	−55	1.75	1.1	1.1	1.3	0.45	0.7	0.75	0.6	0.25	0.8	0.35	2.25
	−78	0.6	0.25	0.4	0.2	0.1	0.2	0.15	0.15	—	0.25	0.1	0.6
900	−55	1.65	1.7	2.15	1.9	—	0.7	0.8	1.0	0.45	0.7	0.7	2.75

[a] See Experimental section.

heated under constant evacuation in the temperature range of −78-20°C after removing the Dewar vessel. Over the range of 20–800°C, the rate of heating was 20°C/min. The pressure was recorded with a thermocouple manometric gauge, and the temperature was measured with a chromel-alumel thermocouple with an accuracy of ±5°C.

RESULTS AND DISCUSSION

Thermal Studies of Rare-Earth Catalysts

All rare-earth catalysts were studied thermally in a stream of nitrogen, helium, and hydrogen. Since the principal characteristics of the decomposition of these hydroxides to give oxides are qualitatively similar, let us first consider the results with neodymium hydroxide (Fig. 1). For comparison, the data for commercial neodymium oxide are also reported.

One can see that the DTA curve (curve 1) shows three endothermic effects. As has already been reported (*4*), the first two peaks are due to dehydration, and the third is caused by two simultaneous processes, namely, dehydration and decomposition of nitrate ions captured by the hydroxide upon precipitation. The results obtained are in quite good agreement with the data of related studies on rare-earth hydroxides in air (*6*, *7*).

The DTA curve of commercial neodymia (Fig. 1, curve 2) which had been kept in air also shows three endothermic effects. The first two peaks are caused (*4*) by dehydration; the last peak has been shown by mass-spectrometric analysis to be due to the evolution of carbon dioxide at 700–820°C. The results of the thermographic study on commercial neodymia indicate abilities to rehydrate in air and to adsorb carbon dioxide.

The thermal curves of zirconium and hafnium hydroxides (Fig. 1) in an inert gas, unlike those of rare-earth hydroxides, show only one endo- and one exothermal effect. The first peak is caused by dehydration, the other by transition of the amorphous dioxide to a crystalline dioxide (*8*, *9*). No effects due to decomposition of nitrate ions have been observed. This is probably due to the fact that, because of their acidity, zirconium and hafnium hydroxides, unlike rare-earth hydroxides, are not capable of forming basic nitrates.

The Effect of the Temperature of Heating and Reduction on Catalytic Activity

The appropriate temperature for heating hydroxides in the range 100–600°C was determined from the data on thermal analysis and from following their activities before and after each of the chemical reactions identified. As a result of these

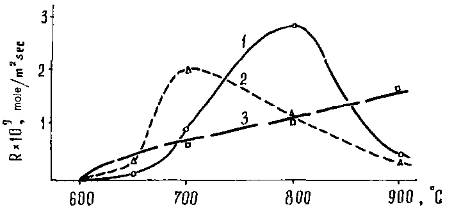


FIG. 2. Effect of the temperature at which oxides have been pretreated *in vacuo* on their activity in ethylene hydrogenation at −78 and −55°C. (1) La_2O_3, −78°C; (2) Nd_2O_3, −78°C; (3) Sm_2O_3, −55°C.

studies, it has been established that trihydroxides and monohydroxides do not catalyze ethylene hydrogenation.

After being heated *in vacuo* at 600°C, the oxides of Sc, Y, and all the rare earths except Ce, Pr, and Tb (see Table 1) began to show catalytic activity. Tb and Pr oxides were activated upon treatment *in vacuo* at a temperature not lower than 800°C. Cerium oxide would not catalyze ethylene hydrogenation, even after being baked at a temperature as high as 900°C. These different behaviors shown by the oxides may be due to the stable tetravalent state of Ce, Pr, and Tb.

The catalytic activities of lanthana and neodymia passed through a maximum as the temperature of heating *in vacuo* was increased (Fig. 2). The activity of the other sesquioxides (Table 1) continuously increased. This specific feature of the behaviors of neodymia and lanthana is due to their ability to undergo polymorphic transformation, in the range of 600–900°C (*10, 11*) from the cubic body-centered (C-form) into the hexagonal (A-form) structure. Among the remaining rare-earth oxides, the C-form is stable under the conditions studied. Thus, one may suggest that an increase in the coordination number of the cation from 6 in the C-form to 7 in the A-form would decrease the catalytic activity. A similar conclusion can be made from the data obtained for nonstoichiometric oxides of cerium, terbium, and praseodymium. Their dioxides have the fluorite structure with the cation coordination number equal to 8, and they do not show any catalytic activity. Terbium and praseodymium oxides begin to show catalytic activity after being heated at 800°C, which may be due to their partial decomposition (*11*). The structure of the resulting oxides is a derivative of the structure of fluorite, but, in its oxygen sublattice, there arises a certain number of anion vacancies, which should result in the appearance, at the surface, of cations with a coordination number less than 8.

Partial hydrogen reduction at 600–800°C (*12*) may be responsible for the activity of cerium dioxide (Table 2). Hydrogen treatment of terbium and praseodymium oxides transforms them into sesquioxides, with a C-type structure of octahedrally coordinated cations, and considerably increases their catalytic activity (Table 2, Fig. 3). On the contrary, hydrogen treatment of erbium oxide insignificantly affected its activity (Fig. 3). The activity changes for Pr_2O_3 as a function of heating (Fig. 3) are similar to those of lanthana and neo-

TABLE 2

The Effect of Hydrogen Treatment Temperature on the Activity of Oxides

Catalyst	Temperature (°C)		Rate ($r \cdot 10^9$ mole/m$^2 \cdot$sec)
	Hydrogen treatment	Experiment	
CeO_2	600	20	1.25
	700	20	7.20
	700	−78	0.0
	800	20	1.30
Pr_2O_3	600	20	0.0
	700	−90	1.0
	700	−101	0.40
Tb_2O_3	600	20	1.25
	700	−55	0.45
	800	−55	1.35
	900	−55	1.45
	900	−67	0.85

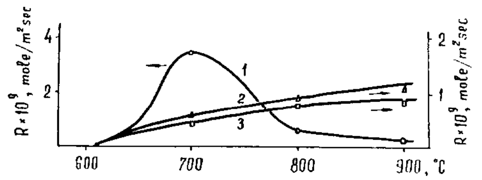


FIG. 3. Effect of the temperature at which oxides have been pretreated in hydrogen on their activity in ethylene hydrogenation at −78 and −55°C. (1) Pr_2O_3, −78°C; (2) Er_2O_3, −55°C; (3) Er_2O_3, −55°C after heating *in vacuo*.

dymia (Fig. 2), since, under these conditions, Pr_2O_3 also undergoes a transformation from the C- into the A-form.

An increase in the catalytic activity of sesquioxides of the C-type structure with an increase in the heating temperature can be explained in two ways: by desorption of an impurity or surface dehydroxylation. For example, Nd_2O_3, prepared from the hydroxide, contained nitrates for which temperature of decomposition is much lower than that of the carbonates present in commercial neodymia. Therefore, the former sample showed catalytic activity after heating at a temperature (600°C) which is 100°C lower than that necessary for the latter. As shown by our measurements, Dy_2O_3 attains maximum activity after heating at 800–900°C. Under these conditions, the oxide surface is 95% dehydroxylated and contains coordinatively unsaturated cations which are likely to be involved in the active centers (*13, 14*) of catalysis.

Variations in Catalytic Activity for the Series of Rare-Earth Oxides

Figure 4 shows the variations in catalytic activity of rare-earth oxides after pretreatment at different temperatures. The temperature of ethylene hydrogenation was 20°C for the samples subjected to treatment *in vacuo* at 600°C, whereas, for the samples pretreated at other temperatures, it was −78°C. Praseodymia and terbia were subjected to hydrogen treatment, followed by treatment *in vacuo* in order to obtain their sesquioxides. According to the data presented, the variation in activity for this series of oxides always depend on the baking temperature; among the samples baked at 600°C, holmia showed the highest activity, and, for praseodymia, lanthana,

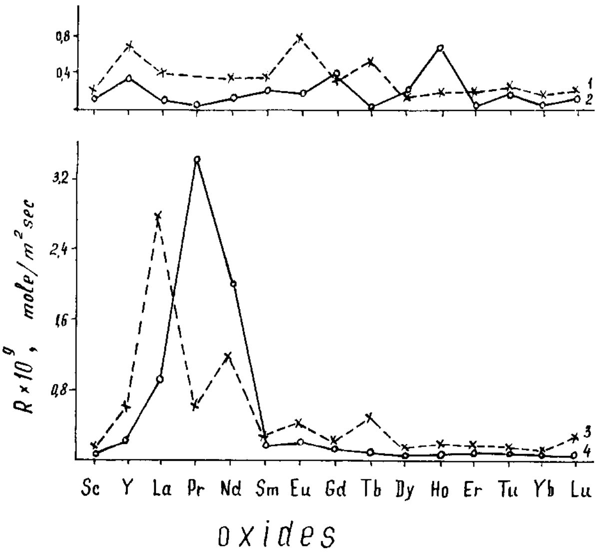


FIG. 4. Activity of Sc, Y, and rare-earth oxides after heating at various temperatures: (1) 900, (2) 600, (3) 800, (4) 700°C.

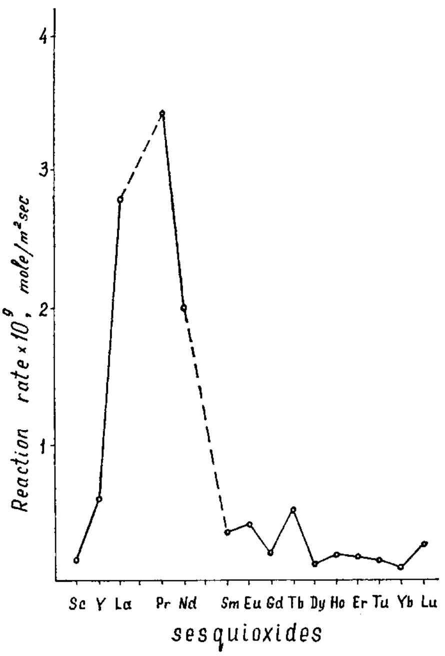


FIG. 5. Activity of Sc, Y, and rare-earth oxides in ethylene hydrogenation at −78°C after heating at temperatures which produced their highest activities.

and terbia, maximum activity is shown after baking at 700, 800, and 900°C, respectively. Thus, maximum catalytic activity is observed at different temperatures of pretreatment for these oxides. These data highlight the difficulty of comparing oxide systems.

Therefore, it seems reasonable to compare the activities of rare-earth oxides after pretreatment at the temperatures at which these oxides exhibit the highest activity. The results (at −78°C) of this comparison are given in Fig. 5. The most active are lanthana and praseodymia, and they are not inferior to chromia which is considered to be the most active oxide catalyst in ethylene hydrogenation (*1*). Moreover, rare-earth oxides exhibit a higher thermal stability than chromia, the activity of which decreases considerably after being heated at temperatures above 600°C. For example, lanthana, after treatment at 800°C, shows high activity at −101 and −116°C ($r = 0.54 \cdot 10^{-9}$ and $0.13 \cdot 10^{-9}$ mole/m²·sec, respectively); the rate of ethylene hydrogenation over chromia under the same conditions is one order of magnitude lower. The activity of the rare-earth sesquioxides varies within one order of magnitude. In this respect, the rare-earth oxides differ considerably from those of the elements of the first transition series, the catalytic activities of which, in ethylene hydrogenation, differ by two or three orders of magnitude (*1*). The most significant variations in activity are observed for the oxides in the series lanthana to gadolinium oxide. The activies of other oxides vary less significantly. The activities of scandia and yttria, like their other chemical properties, proved to be close to those of the yttrium group. At this point, it should be noted that the main chemical properties of the elements of the cerium subgroup vary to a greater extent than those of the elements of the yttrium subgroup (*15*). Comparison of the activities of several pairs of oxides given in Table 3 indicates that catalytic activity is due not only to the electronic configuration of the cation. Theoretical considerations reported in Ref. (*1*) suggest a low activity for scandia, which is not in agreement with the results of this work.

A decrease in the catalytic activity of the oxides from lanthana to lutecia and to

TABLE 3

Hydrogenating Activity of Oxides and Electron Configuration of Cations

Oxide	Electron configuration	Rate of C_2H_4 hydrogenation at −78° ($r \cdot 10^9$ mole/m²·sec)
Sc_2O_3	$3d^0$	0.16
TiO_2		0.0[a]
Y_2O_3	$4d^0$	0.6
ZrO_2		0.0
La_2O_3	$4f^0 5d^0$	2.8
CeO_2		0.0
Lu_2O_3	$4f^{14} 5d^0$	0.25
HfO_2		0.01

[a] According to Ref. (*1*).

scandia (Fig. 5) correlates with a decrease in their basicity (*16*). Moreover, the basic nature of hydrogenating activity is characteristic of a chromia–alumina catalyst, as shown earlier (*17*) by studying the dependence between acidity and toxicity of catalytic poisons. In homogeneous catalysis (*18*), the dependence of the hydrogenating activity of catalysts on their basicity has been established unambiguously.

The observed correlation can be used to explain other experimental results: (i) Acidic oxides (CeO_2, PrO_2, TbO_2, ZrO_2, and TiO_2) are not active catalysts in ethylene hydrogenation; (ii) acidic substances (nitrogen dioxide, carbon dioxide, and water) are catalytic poisons; (iii) there is a change in activity in the series Sc_2O_3, Y_2O_3, La_2O_3, which correlates with the change in basicity.

Mechanism of Ethylene Hydrogenation

The main results obtained from the study of the mechanism of ethylene hydrogenation at −55°C, over dysprosia (*5*) pretreated at 800°C, are given in Table 4. Dysprosia was chosen due to its stability under the conditions studied with respect to both its valence and crystallographic structure.

First, an attempt was made to find out if the hydrogen of the hydroxyl groups on the catalyst surface is involved in reaction 1. For this purpose, deuterium was supplied to the reaction vessel over the sample at −55°C ($P = 4.5$ Torr). After 45 min, the gas was analyzed with a mass spectrometer. Then, the temperature was successively increased to 20, 120, 220, 310, and 410°C. At each temperature, the exchange was carried on for 45 min. The reaction was followed by a variation in the concentration of protium in the gas. It was found that the exchange becomes appreciable at 120°C, and, at 300°C, the reaction practically attains equilibrium. The hydroxyl groups on the Dy_2O_3 surface number about $6 \cdot 10^{17}$ OH groups/m², as determined from the equilibrium ratio of protium and deuterium in the gas phase. The results for reaction 1 show that the hydrogen on OH groups on the catalyst surface, under the conditions used (−55°C), does not exchange with deuterium. The extent of dehydroxylation of the surface is about 95%.

According to the thermodesorption data, hydrogen is adsorbed on dysprosia and erbia in two forms, namely, a "weak" form (w) and a "strong" one (s) which

TABLE 4

Results of Studying the Mechanism of Ethylene Hydrogenation over Dy_2O_3 at −55°C

Reaction	Starting compound	Reaction product[a]
1	$OH_{surf} + D_2$	HD found only at $t \geqslant 120$°C. Equilibrium data at 400°C: 2.5% H_2, 26.5% HD, and 71% D_2. Dy_2O_3 surface dehydroxylated by 95%.
2	$H_{ads}(w + s) + D_2$	HD in negligible amounts.
3	$H_{ads}(s) + D_2$	HD was not found.
4	$H_{ads}(w + s) + C_2D_4$	$C_2D_4H_2$ was not found.
5	$C_2D_{4ads} + H_2$	$C_2D_4H_2$.
6	$C_2H_4 + H_2$	C_2H_6; $r = 0.46 \cdot 10^{-9}$ mole/m²·sec.
7	$C_2H_4 + D_2$	99% $C_2H_4D_2$; $r = 0.30 \cdot 10^{-9}$ mole/m²·sec.
8	$C_2D_4 + H_2$	97% $C_2D_4H_2$; $r = 0.42 \cdot 10^{-9}$ mole/m²·sec.
9	$C_2H_4 + C_2D_4$	HD; $C_2H_{4-x}D_x$; $C_2H_{6-x}D_x$ was not found.
10	$C_2H_6 + D_2$	HD; $C_2H_{6-x}D_x$ was not found.
11	$H_2 + D_2$	HD; $r = 0.38 \cdot 10^{-9}$ mole/m²·sec.
12	$C_2H_4 + H_2 + D_2$ (1.7:1:1) component ratio	47% C_2H_6, 21% C_2H_5D, 32% $C_2H_4D_2$. HD was found after complete ethylene hydrogenation.

[a] The values of the reaction rates are given for 50% conversion.

have different desorption temperatures. Ethane is practically not adsorbed. Over lanthana, which is the most active catalyst in low-temperature ethylene hydrogenation, only a "weak" form of adsorption was found for both hydrogen and ethylene at −78°C. The "weak" form of hydrogen adsorption persists upon evacuation up to 10^{-3} Torr and is removed by evacuation at 10^{-5} Torr.

Reactions 2 and 3 provide evidence for the reactivity of the weakly and strongly adsorbed forms of hydrogen. In these experiments conducted at −55°C, the preadsorbed H_2 was evacuated down to 10^{-3} or 10^{-5} Torr, retaining both or only one strongly adsorbed form of hydrogen, and, then, deuterium was supplied ($P = 0.8$ Torr). After 1 hr, samples were taken for mass-spectrometric analysis. The experiments allowed us to establish that only the weakly adsorbed form of hydrogen is involved in the exchange. No products of adsorbed hydrogen interaction with C_2D_4 were found, according to reaction 4. This shows that the strongly adsorbed hydrogen which makes up about 95% of the total adsorbed hydrogen is not involved in hydrogenation. But we failed to establish the reactivity of the weakly adsorbed hydrogen, since its relative content was about 5%, and, therefore, the amount of ethane which might be formed in this case would be too small to be detected by the technique available. Preadsorbed ethylene was hydrogenated with hydrogen according to reaction 5.

Ethylene hydrogenation with deuterium, according to reaction 7, gives only one isotopic isomer of ethane ($C_2H_4D_2$), which indicates that there is no H–D exchange between hydrocarbon and deuterium. This conclusion is also supported by reactions 8–10 which did not give any evidence for HD formation, isotopic redistribution of hydrogen in the hydrocarbons, variation in the total pressure in reactions 9 and 10, or formation of ethane according to reaction 9 during a period longer than 1 hr. Thus, from reactions 7–10, one may conclude that ethylene hydrogenation over dysprosia at −55°C proceeds via associatively adsorbed ethylene.

When comparing the rates of ethylene hydrogenation according to reactions 6 and 7, it was found that there was a kinetic isotopic effect, with $r_H/r_D = 1.5$. This value is in agreement with the data reported in Ref. (*19*), in which $k_H/k_D = 1.49$ in ethylene hydrogenation over cobalt oxide at 28°C. The deuterium–hydrogen exchange studies (reaction 11) showed that the rates (at −55 and −78°C) and activation energies of H_2–D_2 exchange and ethylene hydrogenation are about the same. This similarity in values of the activation energy or H_2–D_2 exchange over dysprosia were also found by Ashmead *et al.* (*20*). These results allow us to suggest that hydrogen activation is the rate-limiting step of ethylene hydrogenation. There is no kinetic isotopic effect observed when comparing reactions 6 and 8, which is further evidence in support of the above suggestion.

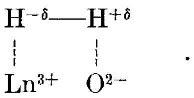
The study of ethylene hydrogenation (C_2H_4) with a nonequilibrium mixture of hydrogen and deuterium, according to reaction 12, demonstrated that in the presence of ethylene the reaction of H_2–D_2 exchange does not occur. This is evidenced by the absence of HD among the reaction products which consisted only of 47% C_2H_6, 21% C_2H_5D, and 32% $C_2H_4D_2$. After completion of ethylene hydrogenation, HD began to accumulate in the reaction products.

Thus, the formation of monodeuteroethane (C_2H_5D), according to reaction 12, with no hydrogen redistribution in the reaction mixture, may indicate that hydrogen atoms add to ethylene successively. This is shown by the following scheme:

$$\begin{array}{lcl} H_2 & & C_2H_4 \\ {\scriptstyle k_1}\downarrow\uparrow{\scriptstyle k_{-1}} & & {\scriptstyle k_2}\downarrow\uparrow{\scriptstyle k_{-2}} \\ H_{2ads}(2H_{ads}) & + & C_2H_{4ads} \xrightarrow{k_3} C_2H_{5ads} \xrightarrow{k_4} C_2H_6. \end{array}$$

Thus, unlike the schemes developed by Horiuti (*21*) and Polyanyi and Rideal and Twigg (*22*) for metallic catalysts, the stage of formation of a semihydrogenated form over dysprosia is irreversible in low-temperature hydrogenation.

The fact that associatively adsorbed ethylene is involved in the reaction implies the suggestion that π complexes can arise on the surface due to a vacant 5*d* orbital in rare earths. According to the latest assumptions, one of the elements in the structure of the active center for hydrogenation is a coordinatively unsaturated cation (*21*). The data we obtained on the dependence (*23*) between catalytic activity and basicity indicate that an electron donor is involved in the active center, and this donor is probably an oxygen ion. According to Ref. (*14*), in this case, hydrogen activation can occur due to the polarizing action of a rare-earth cation (Ln) and an oxygen ion:



$$\begin{array}{cc} H^{-\delta} \text{—} & H^{+\delta} \\ \vdots & \vdots \\ Ln^{3+} & O^{2-} \end{array} .$$

The absence of H_2–D_2 exchange in the presence of ethylene, according to reaction 12, can be explained by the fact that hydrogen and ethylene are adsorbed on the same active centers, and, because of the stronger adsorption of ethylene (20 times as high according to the thermodesorption data), the probability of two hydrogen molecules being situated close to each other is negligible. Therefore, until practically all the ethylene is consumed no H_2–D_2 exchange can take place. Besides, it can be assumed that the rate of interaction between activated hydrogen and adsorbed ethylene would be much higher than that with deuterium.

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