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Studies of Ethylene Hydrogenation and of Adsorbed C_2H_4 and H_2 on Chromia and Lanthana Catalysts

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Adsorbed forms of C_2H_4 and H_2 (and hydrogenation of adsorbed C_2H_4 at −78°C) on Cr_2O_3, $Cr_2O_3 \cdot 7Al_2O_3$, La_2O_3, and Al_2O_3 pretreated at 400–900°C, with increments of 100°C, have been investigated by temperature-programmed desorption. Chemical desorption of the reactants by the catallytic poisons CO, CO_2, and H_2O at −78, −68, and 20°C has been studied on La_2O_3. The hydrogenation activity of these oxides and the control of the poisoning of La_2O_3 in C_2H_4 hydrogenation have been researched by a circulation method at temperatures of −78, −68, and 20°C with an equimolar mixture of C_2H_4 and H_2 at an initial pressure of 10 Torr. The results show that the catalytic activity, the number of adsorbed forms, and the adsorbed amounts of the reactants in the different forms depend on the pretreatment temperature. The distinctiveness of the adsorbed forms of the reactants originates from distinctions in the properties of adsorbed centers. The activity of the catalyst is due to the presence of at least two types of centers on the surface. Different reactivities have been found for different adsorbed C_2H_4 forms in their interaction with H_2 at −78°C. It has been demonstrated that the poisoning effect of CO, CO_2, and H_2O is due to adsorption displacement of the adsorbed hydrogen and ethylene. The ratio between the amount of adsorbed poison and desorbed C_2H_4 and H_2 depends on the chemical nature of the poison.

INTRODUCTION

Ethylene hydrogenation is a suitable test reaction to study the activity of oxide catalysts. Most systems show activity for this reaction. Some oxides are active at low temperatures, which allow studies with "frozen" surfaces, i.e., without complications arising from the oxide surface itself interacting with the reactants. At the present time kinetic and ir studies enable identification of the reaction steps, the nature of the intermediates, and a number of mechanisms for olefin hydrogenation to be specified. A detailed review has been reported (*1*). The available literature data suggest the viability of the programmed thermodesorption approach to kinetic studies of adsorbed reactant species and their surface reactions. The applicability of thermodesorption to the study of adsorbed C_2H_4 and H_2 on Al_2O_3 has been demonstrated by Cvetanovic and Amenomiya (*2*). This technique has been further developed by Reid *et al.* (*3*), who investigated the interaction of C_2H_2 adsorbed species with CO and CO_2 over a Rh/SiO_2 catalyst.

The objective of this work was to study the catalytic activity of La_2O_3 and chromia catalysts in ethylene hydrogenation as a function of the properties of adsorbed C_2H_4 and H_2. This has been done by making TPD studies of adsorbed C_2H_4 and H_2, and by analyzing the products of their surface reaction with catalytic poisons (CO, CO_2, H_2O) for samples of various activity. As a result, a well-defined characterization of the sites for adsorption and catalysis has been established for the systems studied.

EXPERIMENTAL

The alumina was prepared by dehydration of boehmite, the chromia by decomposition of CrO_3 *in vacuo*, and the $Cr_2O_3 \cdot 7Al_2O_3$ catalyst by impregnation of boehmite with CrO_3 followed by heating. Lanthana was prepared by decomposition of the hydroxide. For details one can refer to previous papers (*4, 5*). Before measure-

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ments were made the samples were heated *in vacuo* ($2 \cdot 10^{-5}$ Torr). The temperature of heating was varied from 400 to 900°C with increments of 100°C. The heating rate and the pumping speed were 5°C/min and 0.6 liters/s, respectively.

The catalytic activity was measured in a circulation system (*5*) at temperatures of −78, −68, and 20°C with an equimolar mixture of ethylene and hydrogen at an initial pressure of 10 Torr. The reaction rate at 50% conversion was used as the measure of activity.

The vessel used for thermodesorption studies was connected to a vacuum unit, gas supply, and monopole mass spectrometer MH-7301 (Fig. 1). The heater could be warmed linearly at a rate of 2–16° C/min in the temperature range −180 to 1000°C. Low temperatures were attained by cooling the vessel with cold nitrogen gas. Thermostatic accuracy was 0.5°C for the temperature range −180 to 200°C. The pressure was measured with a thermocouple gauge and an ionization gauge. Adsorption was carried out at −78, −68, and 20°C for 10 min. Adsorption of CO, CO_2, and H_2O was varied by varying the initial pressure in the calibrated volume. For C_2H_4 and H_2 the remaining pressure at the end of adsorption was 5 Torr, and the final pressure did not exceed $3 \cdot 10^{-3}$ Torr for the other gases. After adsorption the samples were evacuated to attain a pressure of $2 \cdot 10^{-5}$ Torr. During the desorption experiment itself, gases were pumped out through the mass spectrometer by an ion pump. The pressure variations as a function of temperature were recorded as thermodesorption (TD) spectra. During thermodesorption the gas pressure in the vessel varied from $2 \cdot 10^{-5}$ to $8 \cdot 10^{-3}$ Torr. The amount of desorbed species was calculated from the TD peak areas following Ehrlich (*6*) as well as from the mass spectrometer results.

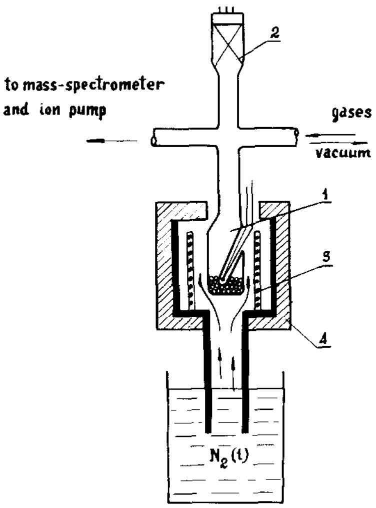

FIG. 1. Illustration of the thermodesorption unit: (1) vessel with catalyst, (2) pressure gauge, (3) heater, (4) thermally insulated copper cylinder.

The compressed C_2H_4 (99.8% v/v purity), H_2 (99.9% v/v purity), and CO_2 (99.6% v/v purity) were purified with a conventional train (PG-1) which included Al_2O_3, a Ni–Cr catalyst, a 4A zeolite, and finally a liquid nitrogen-cooled trap. In addition, C_2H_4 and CO_2 were subjected to low-temperature distilation. Carbon monoxide was passed at −80°C through a 4A zeolite. Water was purified by multiple low-temperature distilations.

RESULTS AND DISCUSSION

1. Adsorbed C_2H_4 and H_2 and Catalytic Activity

Figure 2 shows characteristic TD spectra of C_2H_4 from Cr_2O_3 and $Cr_2O_3 \cdot 7Al_2O_3$ catalysts which were pretreated at various temperatures. It is seen that C_2H_4 can be desorbed in three forms: a low-temperature α-form, with a temperature maximum in the range −40 to −10°C, and in two high-temperature β- and γ-forms, with maxima in the range 50 to 100°C and 350 to 400°C, respectively. It has been demonstrated mass spectrometrically that α- and β-forms correspond to ethylene desorption and the γ-form to butene desorption.

Table 1 shows the amount of C_2H_4 and H_2 adsorbed in different forms. The data allow us to conclude that the number of adsorbed C_2H_4 species is dependent on the nature of

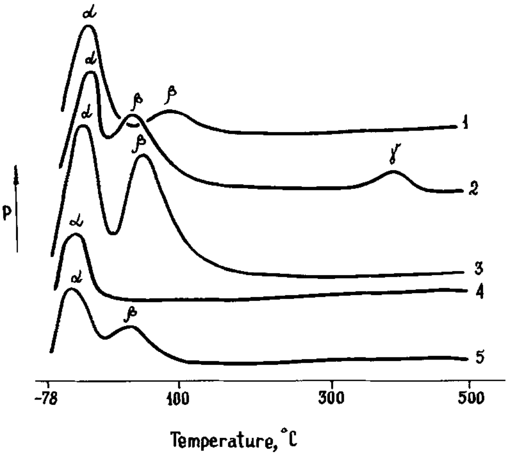

FIG. 2. TD spectra of adsorbed C_2H_4 (P_{ads} = 5 Torr, T_{ads} = 5 min, t_{ads} = −78°C) after heating at various temperatures. Cr_2O_3: (1) 400°C, (2) 600°C, (3) 800°C; $Cr_2O_3 \cdot 7Al_2O_3$: (4) 400°C, (5) 600°C.

the catalyst and the temperature at which it had been heated prior to adsorption. In the case of chromia, α- and β-species were observed after heating at 400°C. For the other samples heated at 400 and 500°C only the α-form was observed. The β-form was found when the temperature was increased to 600°C. The relative amount of each form is dependent on the nature of the catalyst and the thermal treatment. For example, over La_2O_3 98% of the ethylene was adsorbed as the α-form. In the case of Cr_2O_3, after heating at 800°C, the amounts of ethylene in the α- and β-forms were almost equal. The amount of adsorbed C_2H_4 was greatly dependent on the heating temperature. For all the samples in the temperature range studied, one could observe a strong dependence of the amount adsorbed on temperature, with a maximum for La_2O_3 at 700°C and for the other samples at 800°C.

The TD spectra of hydrogen over Cr_2O_3 and $Cr_2O_3 \cdot 7Al_2O_3$ showed α- and β-forms whereas over La_2O_3 and Al_2O_3 only α-forms were found (Table 1). The temperature ranges for the maxima in the α- and β-forms

TABLE 1

Effect of Pretreatment Temperature on the Amount of Adsorbed C_2H_4 and H_2 (10^8 moles/m^2) and C_2H_4 Hydrogenation rate, *r* (10^8 moles/m$^2 \cdot$ s)[a]

Catalyst	Adsorbed forms of C_2H_4 and H_2	Pretreatment temperature (°C)					
		400	500	600	700	800	900
Cr_2O_3[b]	α-C_2H_4	39.2	44.3	49.8	70.7	147.7	121.8
	β-C_2H_4	2.6	4.2	36.5	68.6	123.7	75.7
	α-H_2	0	1.8	2.9	7.9	14.4	15.5
	β-H_2	0	0.2	0.4	11.3	44.1	33.2
	r	0	0	1.0	5.5	10.2	1.3
$Cr_2O_3 \cdot 7Al_2O_3$	α-C_2H_4	10.1	8.3	10.9	12.5	13.8	13.6
	β-C_2H_4	0	0	1.2	4.6	6.2	5.3
	α-H_2	0	0.3	5.8	7.2	7.3	5.5
	β-H_2	0	0.1	1.2	1.3	2.2	1.1
	r	0	0	0.2	0.4	0.6	0.8
Al_2O_3	α-C_2H_4	1.1	7.2	6.1	5.9	7.8	9.2
	β-C_2H_4	0	0	0.5	1.6	3.9	3.8
	α-H_2	0	0.1	0.2	0.4	0.4	0.3
	r	0	0	0	0	0	0
La_2O_3	α-C_2H_4	12.3	14.6	15.2	17.2	16.8	16.4
	β-C_2H_4	0	0	0.1	0.4	0.3	0.3
	α-H_2	0	0.1	0.8	3.6	2.4	0.9
	r	0	0	0.2	2.8	1.9	0.2

[a] Hydrogenation rate was measured in a circulation system. Temperature of adsorption and reaction: −78°C.

[b] After heating at 500–700°C, the γ-form, amounting to 30% of the total amount of the C_2H_4 adsorbed, is found.

of H_2 were -50 to $-10°C$ and 20 to 60°C, respectively. The temperature at which H_2 adsorption began was 500°C, compared to 400°C for C_2H_4 adsorption. For the chromia–alumina catalyst, most of the H_2 was adsorbed as the α-form at all heating temperatures. In the case of chromia, heated at 500 and 600°C, hydrogen was adsorbed mainly as the α-form. As with C_2H_4, the maximum in H_2 adsorption occurred over La_2O_3 after heating at 700°C. For the other samples the temperature was 800°C. According to the total amount of H_2 adsorbed, the systems studied can be ordered in the following series: $Cr_2O_3 > Cr_2O_3$ $7Al_2O_3 > La_2O_3 > Al_2O_3$. The specific activities of Cr_2O_3 and La_2O_3 in ethylene hydrogenation at $-78°C$ attain their maximum (Table 1) at catalyst pretreatment temperatures of 800 and 700°C, respectively. For the $Cr_2O_3 \cdot 7Al_2O_3$ catalyst, one could observe a monotonic growth of activity with an increase of heating temperature. In the temperature range studied alumina did not catalyze the reaction.

From Table 1 one can conclude that there is a correlation between the amount of C_2H_4 and H_2 adsorbed and the activity of La_2O_3 and Cr_2O_3. In the case of the chromia–alumina catalyst, a correlation is observed in the temperature range 400–800°C. In accordance with the above dependence, the lack of Al_2O_3 activity may be qualitatively accounted for by the insignificant amount of H_2 which is adsorbed. The observed correlation between activity and adsorption, however, does not allow a quantitative estimate. To illustrate this, the samples of chromia heated at 600 and 900°C show great differences in the amount of adsorbed C_2H_4 and H_2, but display similar catalytic activity. The activity of Cr_2O_3 heated at 800°C is 5.4 times greater than that of La_2O_3, whereas the ratio of the adsorbed amounts of C_2H_4 is equal to 15.9 and that of H_2 is equal to 25.2. No strict functional dependence was observed between the activity and the amount of adsorbed H_2 and C_2H_4 in any of the adsorbed forms studied. The lack of quantitative dependence between the activity and adsorption capacity of the catalysts suggests something about the nature of the catalyst. According to Ehrlich (*6*) the thermodesorption technique enables one to distinguish the adsorbed forms according to the heat values of their interaction with the surface. The degree of their involvement in catalysis may depend on their lability which, in turn, has a very complicated dependence on the thermal values characteristic of these forms.

2. *Hydrogenation of Adsorbed C_2H_4 and Interaction of Adsorbed Hydrogen with Deuterium.*

Figure 3 shows the TD spectra of C_2H_4 for chromia and chromia–alumina catalysts and the effect of hydrogen treatment at $-78°C$ for 30 s. In the case of Cr_2O_3, one can observe hydrogenation of the β-form, and, in the case of chromia–alumina and also for lanthana catalysts, one can observe hydrogenation of the α-form of the adsorbed C_2H_4. The data obtained illustrate some differences in the reactivity of the adsorbed species. For the samples studied the temperature maxima of the α- and the β-forms were about the same, and hence on each catalyst these forms might possess equal energies of surface binding. The difference in reactivity is most probably due to the differing nature of the catalysts. The amount of C_2H_4 consumed was determined by comparing its TD spectrum before and after H_2 treatment. The hydrogenation rate of adsorbed C_2H_4 was calculated from the dependence of the coverage of the catalyst surface by C_2H_4 on exposure time in the presence of 5 Torr H_2. In the case of the chromia–alumina catalyst, with a fractional surface coverage of C_2H_4 equal to 0.007, the rates were $1.1 \cdot 10^{-8}$ and $9.9 \cdot 10^{-8}$ mole/$m^2 \cdot s$ after preheating at 600 and 800°C, respectively. This variation in the hydrogenation rate (9 times) corresponds to a variation in the amounts of adsorbed C_2H_4 of 1.2 times and adsorbed H_2 of 1.3 times. The results obtained show that variations in the heating temperature affect not only the amounts of reactants adsorbed, but also their reactivity.

Moreover, an effect of the heating temperature in the range 600–800°C on the exchange reactivity of the adsorbed hydrogen with deuterium has been observed ($P_{D_2} = 5$ Torr at -78°C, exposure time = 5 min, La_2O_3). These results are given below in the form of the amount of HD found to be desorbed in the TD experiment. Included from Table 1 for comparison are the rate of C_2H_4 hydrogenation and the amount of hydrogen adsorbed. The data show that there is a correlation between La_2O_3 activity in H–D exchange and in hydrogenation of C_2H_4 at -78°C:

	Temperature (°C)		
	600	700	800
Amount of absorbed H_2 ($\times 10^8$ moles/m^2)	0.8	3.6	2.4
Amount of desorbed HD ($\times 10^8$ moles/m^2)	0.04	1.0	0.3
Hydrogenation rate of C_2H_4 ($\times 10^8$ moles/m$^2 \cdot$ s)	0.2	2.8	1.9

Therefore, the activity of La_2O_3 for hydrogenation of C_2H_4 may be associated with its ability to activate a hydrogen molecule.

3. *Interaction of Adsorbed C_2H_4 and H_2 with the Catalytic Poisons CO, CO_2, and H_2O over Lanthana*

Table 2 lists the reactions of adsorbed C_2H_4 and H_2 with the catalytic poisons CO, CO_2, and H_2O and the reactions of the adsorbed poisons with C_2H_4 and H_2. The amount of the poisons used was sufficient for complete poisoning of the catalysts (see below). In all cases the amounts of the adsorbed substances are related to 1 m^2 of the surface ($S_{sp} = 20$ m^2/g). The amount of the second reactant is expressed in molar units.

It is demonstrated that as a result of poisoning, preadsorbed C_2H_4 at room temperature (reaction 1–3) is completely displaced. To displace a C_2H_4 molecule at room temperature 16 molecules of CO, or 79 molecules of CO_2, or 135 molecules of H_2O are needed. With a smaller amount of the poison, the displacement of C_2H_4 was incomplete. With $1200 \cdot 10^{-8}$ mole H_2O (corresponding to a relative catalyst activity of 0.6), $8.5 \cdot 10^{-8}$ mole of C_2H_4 was displaced, i.e., 50% of the preadsorbed C_2H_4. At room temperature no C_2H_4 was adsorbed onto a completely poisoned catalyst (reactions 4–6). With a partially poisoned catalyst, one could observe C_2H_4 adsorption but to a smaller extent than with a nonpoisoned one. For example, a partially CO_2-poisoned catalyst (with a relative activity of 0.7) affected ethylene chemisorption in the amount of $1.2 \cdot 10^{-8}$ mole/m^2, which is 70% of the adsorbed amount on a nonpoisoned catalyst.

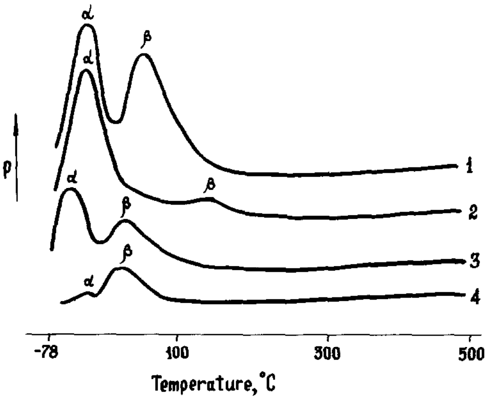

FIG. 3. TD spectra of C_2H_4 before and after H_2 treatment at -78°C. (1) TD spectrum of C_2H_4 on Cr_2O_3 pretreated at 800°C; (2) TD spectrum of C_2H_4 on Cr_2O_3 (as above) after catalyst was treated with H_2 at -78°C for 30 sec; (3) TD spectrum of C_2H_4 on $Cr_2O_3 \cdot 7Al_2O_3$, catalyst pretreated at 800°C; (4) TD spectrum of C_2H_4 on $Cr_2O_3 \cdot 7Al_2O_3$ (as above) after treated with H_2 at -78°C for 30 s.

At low temperatures no displacement of preadsorbed C_2H_4 by CO and CO_2 was observed (reactions 7 and 8). Preadsorption of poison in an amount sufficient for complete poisoning did not affect C_2H_4 adsorption. As much C_2H_4 adsorbed as on a nonpoisoned catalyst (reactions 9–10). In this case, TD spectra and mass spectrometric analysis show displacement of some of the adsorbed poisons. For instance, in experiment 9 TD

TABLE 2

Reactions of Absorbed Species on La_2O_3

Reaction No.	Temperature (°C)	Reactant		Reaction products	
		Absorbed species (moles/m^2 · 10^8)	Introduced into vessel[a] (moles · 10^8)	Absorbed species (moles/m^2 · 10^8)	Gas phase (mole · 10^8)
			1		
1	20	C_2H_4(1.7)	CO(270)	CO(27) C_2H_4(0.1)	C_2H_4(16)
2	20	C_2H_4(1.7)	CO_2(1340)	CO_2(134) C_2H_4(0.1)	C_2H_4(16)
3	20	C_2H_4(1.7)	H_2O(2300)	H_2(230)	C_2H_4(17)
4	20	CO(27)	C_2H_4(4100)	No displacement	
5	20	CO_2(134)	C_2H_4(4100)	No displacement	
6	20	H_2O(230)	C_2H_4(4100)	No displacement	
7	−78	C_2H_4(16.9)	CO(410)	No displacement	
8	−68	C_2H_4(11.9)	CO_2(1370)	No displacement	
9	−78	CO(41)	C_2H_4(4100)	CO(31) C_2H_4(16.9)	CO(100)
10	−68	CO_2(137)	C_2H_4(4100)	CO_2(129) C_2H_4(11.9)	CO_2(80)
11	−78	H_2(2.9)	CO(410)	CO(41)	H_2(29)
12	−68	H_2(1.8)	CO_2(1370)	CO_2(137)	H_2(18)
13	−78	CO(41)	H_2(4100)	No displacement	
14	−68	CO_2(137)	H_2(4100)	No displacement	

[a] Volume of the vessel: 150 cm^3.

shows that of the original $41 \cdot 10^{-8}$ mole/m^2 of CO that was adsorbed, only $31 \cdot 10^{-8}$ mole/m^2 remains after contact with gas-phase C_2H_4. This difference allows us to conclude that $100 \cdot 10^{-8}$ mole of CO was displaced. It should be noted that the accuracy of the measurements in these experiments was low, with an error of 20%.

Further TD studies (*7*) have shown the existence of a temperature effect on the equilibrium state of the interaction between adsorbed C_2H_4 and CO or CO_2. The results can be understood by considering that there is a transition at high temperatures from weakly chemisorbed species to strongly chemisorbed ones.

Preadsorbed H_2 was completely displaced by poisons at low temperatures (reactions 11–12). Comparison of the amount of H_2 displaced with the amount of the poison adsorbed shows that displacement of a H_2 molecule requires 14 molecules of CO or 76 molecules of CO_2. In the case of preadsorption of CO or CO_2, no H_2 adsorption was observed (reactions 13 and 14).

These poisoning studies imply that the activity loss shown by doping the surface of La_2O_3 with CO, CO_2, H_2O results from a loss in the ability of the catalyst to chemisorb H_2.

4. *Regularities in Catalyst Poisoning by H_2O, CO, and CO_2.*

Figure 4 shows isotherms for the poisoning of La_2O_3 with water vapor, carbon monoxide, and carbon dioxide. The temperature of adsorption of the poison was varied in the experiments. The catalytic activity is given in relative units. On the unpoisoned catalyst the rates of C_2H_4 hydrogenation (*r*) were as follows:

	Temperature (°C)		
	20	−68	−78
r ($\times 10^8$ moles/m^2 · s)	6.5	2.9	2.0

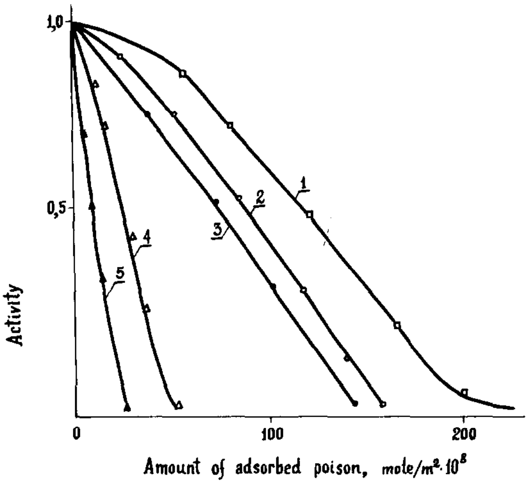

FIG. 4. Isotherms of La_2O_3 poisoning in C_2H_4 hydrogenation at temperatures of 20, −68, and −78°C. (1) H_2O, 20°C; (2) CO_2, −68°C; (3) CO_2, 20°C; (4) CO, −78°C; (5) CO, 20°C.

The amount of the poisons used in the experiments corresponded to the following degrees of coverage: CO, from 0 to 0.025; CO_2, from 0 to 0.145; H_2O, from 0 to 0.216. Figure 4 shows that with small to moderate amounts of the poisons, there is a linear dependence between the catalytic activity and the amount of the poison adsorbed. At the temperatures studied the following series of specific toxicity could be observed: CO > CO_2 > H_2O. This suggests that the adsorption selectivity of the above poisons with respect to the catalytically active centers is different. It should be noted that with equal amounts of the same poison, the degree of poisoning is dependent on the adsorption temperature. Heating a partially poisoned catalyst (with a relative activity of 0.5) from 20 to 80°C results in a complete loss of activity. This indicates that under the conditions studied chemisorption of the poison is not at equilibrium. It seems likely that even with only partial filling of the centers having high adsorption energy, some of the molecules are adsorbed on weak centers. Therefore, an assumption is made that catalytic activity is due to the centers strongly adsorbing the poison molecules. Given below are the fractional areas of the active surface (θ) calculated from the poisoning isotherms and the minimum amount of poison necessary for complete poisoning of the catalyst at each temperature studied. To calculate θ the sizes of elementary sites were taken from the literature (*8*):

	Poison							
	CO		CO_2		H_2O	C_2H_4		H_2
t (°C)	20	−78	20	−68	20	20	−78	−78
θ[1]	0.014	0.025	0.132	0.145	0.216	0.003	0.024	0.002

These data indicate that the number of active centers of poison chemisorption has been estimated approximately.

To conclude, the results obtained give the following values for relative toxicity of the poisons:

H_2O	CO_2	CO
1	1.65	15.2.

CONCLUSIONS

The appearance of more than one peak in a TD spectrum of adsorbed C_2H_4 or H_2 on Al_2O_3, La_2O_3, or chromia–alumina catalyst when the temperature at which the catalyst has been pretreated is increased means that these catalysts possess at least several types of adsorption centers. For ethylene adsorption we may assume there are three types which can be designated in accordance with the adsorbed forms as A-, B-, and C-adsorption centers. In the case of hy-

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[1] For C_2H_4 and H_2 the extent of surface filling is calculated from the TD spectra.

drogen we may likewise assume two types of adsorption center. Moreover, the onset of hydrogen adsorption itself is observed at a pretreatment temperature higher than that for ethylene adsorption. This shows that A-centers for ethylene adsorption are not capable of hydrogen adsorption. Hydrogen is likely to be adsorbed on the B- or C-centers, which are active in C_2H_4 adsorption, or on other surface sites showing no C_2H_4 adsorption.

Certain conclusions about the nature of the adsorption centers can be made from the data on the interaction of adsorbed C_2H_4 and H_2 with catalytic poisons. The most toxic of the poisons, carbon monoxide, which shows a higher selectivity for being adsorbed on those adsorption sites important for ethylene hydrogenation as compared with CO_2 and H_2O, interacts with coordinatively unsaturated cations. Thus it appears that catalyst adsorptivity depends on these cations. The technique used in these experiments did not allow us to show what the differences are between the A-, B-, and C-centers. The hypothesis we advanced earlier (*1, 10*) concerning the dependence of the activity of oxide systems on basicity suggests involvement of oxygen ions in the adsorption centers, which is also assumed in (*11*). The data presented and the assumption made by Peri (*12*) allow a conclusion that A-centers are isolated coordinatively unsaturated cations. B- and C-centers may be groups of two to three vacancies or two to three oxygen ions. The presence of these formations was shown for Al_2O_3 (*12, 13*).

The data obtained demonstrate that the catalysts can adsorb ethylene after heating at temperatures lower than those necessary for catalytic activity. Therefore the presence of A-centers alone is insufficient for catalytic activity to manifest itself. Thus, for hydrogenation it is necessary to activate not only the olefin double bond but also a hydrogen molecule. No activation of the latter by A-centers takes place.

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