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Hydrogenation of Ethylene on Alumina After Hydrogen Spillover

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Hydrogen is adsorbed on alumina in the presence of a nickel-on-alumina catalyst. After the removal of the catalyst, ethylene in a hydrogen–ethylene mixture is converted into ethane at 25 or 110°C. The amount of ethane formed is much higher than the amount of hydrogen initially adsorbed on alumina. The reaction is therefore of a catalytic type utilizing hydrogen from the gas phase, instead of a simple addition to ethylene of the hydrogen preadsorbed on alumina. A chain mechanism of this catalytic hydrogenation is proposed.

INTRODUCTION

It has been shown in the first paper of this series (*1*) that an alumina aerogel which was previously in contact with a nickel-on-alumina aerogel catalyst at 300°C, in the presence of 700 Torr of hydrogen, is able to convert ethylene into ethane at room temperature, after the catalyst has been withdrawn and isolated. As this reaction is not observed with the alumina aerogel submitted to hydrogen at 300°C, but in the absence of the catalyst, it was concluded that the aptitude for hydrogenation of ethylene is conferred on alumina by adsorbed hydrogen which migrated over alumina from nickel sites of the catalyst.

Particular attention must be given to an eventual migration of nickel from the catalyst to the alumina in order to confirm that hydrogen spillover is responsible for the observed effects. In a recent review paper concerning hydrogen spillover Sermon and Bond (2) gave a thorough account of all experimental features and limitations of hydrogen migration from the metal to the support. It appears from this review that a direct catalytic demonstration of this spillover has not yet been reported.

EXPERIMENTAL METHODS

The Pyrex reactor used in this work is of the type already described (*1*) and is shown in Fig. 1. The catalyst (30 mg) is placed on the bottom of a pyrex nonporous pan (A) and is covered by 1 g of alumina aerogel (C) held in a Pyrex holder (D) with a porous glass bottom. This holder can be easily removed from the reactor in order to change the sample of alumina. The lifting device (H) allows the removal of the catalyst (with some alumina) in the pan, which is suspended by an inert wire and glass rod (I) and takes the position (B). The purpose of the stopcock (F) is to isolate the catalyst in the pan from alumina at (C) during the catalytic run with ethylene. The vacuum line and the gas supplies are connected through the stopcock (G). The reactor may be heated by the oven (J). A recirculation pump (K) is provided for homogenization of the gas mixture. The liquid nitrogen trap (L) is included in the circuit agitated by the pump. A calibrated volume (M) allows calculation of the volume of the reactor parts and also the introduction of a known amount of ethylene into the reactor. Sampling for the gas chromatographic

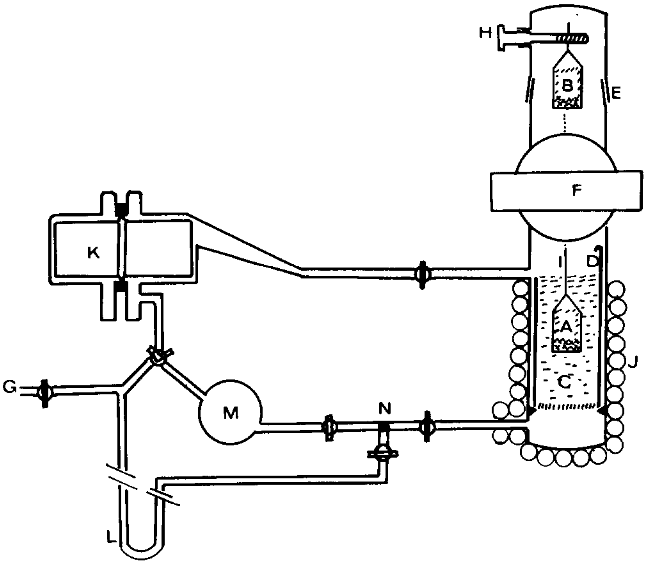

FIG. 1. Reactor for the spilt-over hydrogen reaction.

analysis is made through the device (N).

The description of the alumina aerogel and of the nickel-on-alumina aerogel catalyst was given previously (*1*). It is recalled that this alumina is amorphous and that it contains OCH_3 groups due to the conditions of its preparation in an autoclave (evacuation of methanol which is the solvent of aluminum *sec*-butylate, in hypercritical conditions). The nickel content of the alumina aerogel is 33 ppm, this impurity being introduced by the aluminum alcoxide which is hydrolyzed into alumina in the autoclave. In order to insure that this nickel was not involved in the hydrogenation of ethylene, some experiments were performed for this purpose. Silicone grease was used for stopcocks and joints, as the presence of methoxy groups in alumina invalidates any precautions concerning the introduction of carbonaceous material.

The following procedure was employed throughout. The catalyst in the pan, in position (A), immersed in alumina, is first evacuated (10^{-6} Torr) at 350°C during 24 hr and then submitted to hydrogen (760 Torr) at 300°C for at least 8 hr. The reactor is then cooled to a desired temperature and the pan containing the catalyst is lifted to the position (B). It is impossible to lose any catalyst particles since they cover only the bottom of the pan. The stopcock (F) is then closed in order to isolate the catalyst from the reactor which now only contains alumina. Ethylene (50 cm^3) in the volume (M) is introduced into the system where its partial pressure in the reactor is approximately 100 Torr and the formation of ethane is monitored by gas chromatography.

RESULTS AND DISCUSSION

It has been observed previously that the adsorption of hydrogen by the nickel-on-alumina aerogel catalyst increases when the temperature increases from 25 to 110°C and finally to 300°C. The amount of hydrogen (STP) adsorbed at 760 Torr and 300°C is of the order of 160 cm^3/g Ni which would correspond to a metallic surface of 545 m^2/g Ni or to a nickel crystallite diameter of 12.5 Å. Magnetic measurements showed, on the contrary, that the mean diameter of nickel particles was of the order of 70 Å (*3*). It is therefore doubtful that the total amount of hydrogen

(160 cm^3) is adsorbed only on nickel sites, whereas its migration onto alumina support would explain the discrepancies (5–6-fold) between the two values of the diameter of the nickel particles.

The amount of hydrogen adsorbed by alumina was determined volumetrically using a mixture containing 30 mg of the catalyst and 1 g of alumina. Taking into account the amount of hydrogen adsorbed by the catalyst, determined previously, it appeared, by subtraction, that alumina (1 g) adsorbs reversibly at 760 Torr 2.5 cm^3 of H_2 at 300°C, 1.3 cm^3 at 110°C and 0.5 cm^3 at 25°C. No hydrogen adsorption was detected at the temperatures listed when alumina did not contain the catalyst. These results show that hydrogen is adsorbed on alumina provided metallic nickel is also present.

1. Influence of Time of Hydrogen Treatment of Alumina

Since the amount of hydrogen held by alumina decreases with the decrease in temperature, the experiments of the hydrogenation of ethylene, in the reactor of Fig. 1, were performed after hydrogen treatment (700 Torr), in the presence of the catalyst in the pan at 300°C, for at least 8 hr, and afterwards cooling to 25°C either directly, or with an intermediate stop at 110°C. The catalyst was finally lifted and isolated, and 50 cm^3 (STP) of ethylene were introduced at 25°C. The reaction was followed by gas chromatography at two temperatures: 25 and 110°C. Table 1 summarizes the results.

If the temperature of the reaction is raised to 300°C the transformation into ethane of 50 cm^3 of ethylene initially introduced is complete, in each case, after 5 hr of reaction.

The results in Table 1 show that the rate of cooling and also the time length of various steps influences the volume of ethylene hydrogenated. The comparison of Expts 1 and 3 on the one hand with 2 and 4 on the other hand indicates that the volumes of ethane formed at 110°C are almost proportional to the cooling time from 300 to 25°C. The time length of the treatment in hydrogen at 300°C does not seem to play any significant role if it is extended beyond 8 hr. The most significant value is the conversion of 16.6 cm^3 of ethylene into ethane after 20 hr at 110°C for Expt 3 in which an 8 hr stop at 110°C preceded the final cooling to 25°C. Taking into account the fact that the amount of hydrogen fixed

TABLE 1

ETHYLENE HYDROGENATION ON ALUMINA

Expt no.	Time of H_2 treatment at 300°C (hr)	Time of cooling to 25°C (hr)	Time of H_2 treatment at 25°C (hr)	Temp of reaction with ethylene during 20 hr (°C)	Amount of ethane formed per 1 g Al_2O_3 (cm^3)
1	8	1	14	25 110	0.015 2.5
2	13	1	0	25 110	0.015 0.5
3	13	8 at 110°C 1 at 25°C	15	25 110	0.025 16.6
4	16	0.1	0	25 110	0.03 0.06

on alumina decreases when the temperature decreases and that the rate of reaction also decreases, the best conditions which seem to prevail for the hydrogenation of ethylene are: (i) hydrogen treatment at 300°C during 8–13 hr, (ii) cooling in hydrogen to 110°C and maintaining the catalyst at this temperature for 8 hr without further cooling to 25°C, (iii) withdrawal of the catalyst and introduction of 50 cm^3 of ethylene for reaction at 110°C. By applying these conditions it was found that almost 45 cm^3 of ethane, instead of 16.6 cm^3, were formed in 20 hr. This procedure will be referred to as a standard activation procedure of alumina. Finally, we also studied whether the total hydrogenation of ethylene after 5 hr at 300°C is consecutive to the activation procedure of alumina in the presence of the catalyst, or whether it can be achieved without this previous activation.

2. *Reactions on Activated and Nonactivated Aluminas*

The activation procedure was that adopted for Expt 3 of Table 1. Three samples of alumina were involved in each case: (i) alumina aerogel which was not submitted to the catalyst (blank L), (ii) alumina aerogel which contained the catalyst during the activation procedure (test M, identical to Expt 3 of Table 2), (iii) the alumina from the test M, after having converted ethylene to ethane, afterwards degassed at 300°C and again submitted to hydrogen at 300°C, but without the catalyst (test N). The results are summarized in Table 2.

These values clearly show that at all temperatures when the reaction is almost complete the amount of ethane ($t = 20$ hr at 25 and 110°C, $t = 5$ hr at 300°C) formed on alumina M which was activated in the presence of the catalyst, is always higher than that formed on the two other samples (L and N). The activation energy in the formation of ethane on alumina M, calculated from values in Table 2 (for $t = 20$ hr) at 25 and 110°C, is of the order of 17 kcal/mole. It must be recalled that the activation energy in the hydrogenation of ethylene on alumina varies between 15 and 27 kcal/mole (*4*) and that the activation energy for the same reaction on nickel deposited on alumina is 8.2 kcal/mole (*5*).

TABLE 2
REACTION ON ACTIVATED AND NONACTIVATED ALUMINAS

Temp of reaction with ethylene (°C)	Sample	Amount (cm^3) of ethane formed per 1 g of Al_2O_3 after a reaction time t		
		$t = 2$ hr	$t = 5$ hr	$t = 20$ hr
25	L	10^{-3}	10^{-3}	10^{-3}
	M	4×10^{-3}	6×10^{-3}	25×10^{-3}
	N	2×10^{-3}	2×10^{-3}	2×10^{-3}
110	L	3.6×10^{-3}	5×10^{-3}	5×10^{-3}
	M	8×10^{-3}	0.17	16.6
	N	0.2	0.3	0.35
300	L	27.6	37	—
	M	24.5	50	—
	N	24.5	37	—

The sample L (blank) which was activated in hydrogen at 300°C, but in the absence of the catalyst, shows a negligible activity up to 110°C, but a quite considerable one at 300°C. This result indicates that alumina aerogel is a good conventional (*6*) catalyst for this reaction at 300°C, with an activity comparable to that, at 400°C, of delta-alumina activated in vacuum (*4*). But the comparison of the activities after 20 hr at 110°C of samples L (blank – 5×10^{-3} cm^3 C_2H_6) and M (activated in the presence of catalyst – 16.6 cm^3 C_2H_6) leads to the conclusion that the activation procedure in the presence of the catalyst is responsible for some favorable modifications of alumina M.

Alumina N derives from alumina M as previously indicated. A second activation in hydrogen at 300°C, but in the absence of the catalyst, of the alumina M, gives alumina N whose activity after 20 hr at 110°C (0.35 cm^3) is barely comparable to that of the initial active solid M (16.6 cm^3). The evacuation at 300°C of alumina M after the first test produced some unfavorable modifications which are not compensated by a hydrogen treatment at 300°C in the absence of the catalyst. If the migration of nickel from the catalyst to the alumina M was responsible for the high catalytic activity of this sample (16.6 cm^3), an activity of the same order of magnitude should be observed after the alumina M is converted into alumina N. The analysis of nickel content by atomic absorption spectroscopy shows indeed that sample L (blank) contains 33 ppm of nickel (not necessarily metallic), whereas alumina M, which has been in contact with the catalyst, contains 20 ppm of this element. Clearly, nickel cannot be considered as responsible for the catalytic activity of sample M. When alumina M is examined by ESR, no metallic nickel is detected on this sample, the detection threshold being of the order of 1 ppm.

Finally, the results of Table 2 for sample M at 110°C give some indication of the presence of an induction period in the hydrogenation of ethylene. Figure 2 shows the kinetics of the formation of ethane during the three tests at 110°C. The reaction was followed during the first 5 hr and then after 19 hr. In the case of sample L (blank) the rate of the reaction seems to be constant, as for sample N (after the first 2 hr), whereas sample M shows a noticeable acceleration of the reaction after the first 5 hr. The same trend is always observed for all reactions registered on alumina activated in the presence of the catalyst (see Fig. 3, discussed below).

3. *Influence of Hydrogen Adsorbed on Alumina*

It has been previously mentioned that hydrogen is reversibly adsorbed on alumina mixed with the catalyst, the amount decreasing as the temperature of hydrogen adsorption decreases. In all experiments

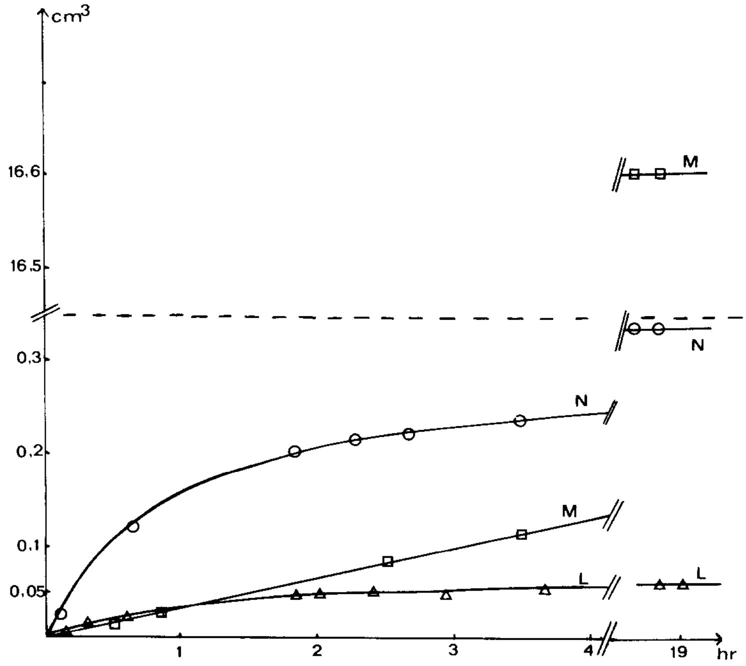

FIG. 2. Hydrogenation of ethylene at 110°C on alumina samples of Table 2: (△) alumina L (blank), (□) alumina N (with spilt-over hydrogen), (○) alumina N (sample M degassed and treated with H_2 at 300°C without the catalyst).

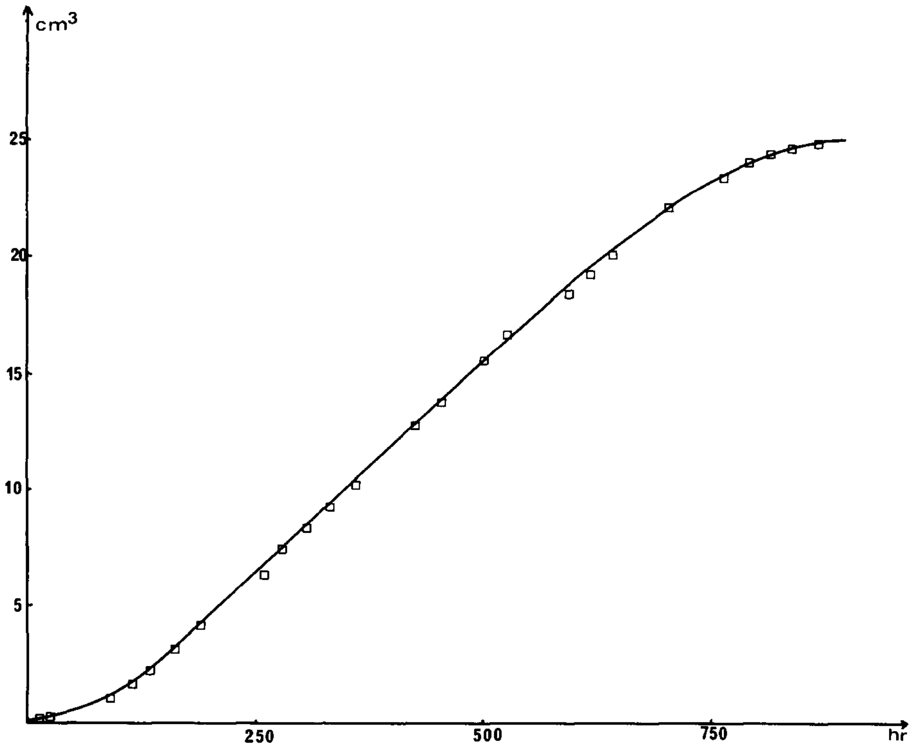

FIG. 3. Hydrogenation of ethylene at 25°C on demethoxylated alumina.

described below, the standard activation procedure of alumina was used and the catalytic activity was tested at 110°C.

If, after this activation, hydrogen is evacuated at 110°C for 2 hr and the reaction mixture (hydrogen + 50 cm^3 of C_2H_4) then introduced onto alumina, only a negligible amount of ethane is found after about 20 hr, instead of 45 cm^3 as before. Hydrogen which was first reversibly adsorbed on alumina by spillover from the catalyst, is desorbed during the evacuation. Simultaneously, the catalytic activity towards a mixture of H_2 and C_2H_4 is suppressed. This experiment shows therefore that the spilt-over hydrogen is an essential factor in the catalytic activity and also that the migration of nickel from catalyst to alumina is excluded. If not, alumina should be active even after evacuation of hydrogen at 110°C.

If after the first reaction at 110°C (45 cm^3 of ethane formed in about 20 hr) the reactor is flushed at 110°C by hydrogen, in order to evacuate the reacted gases, and if again 50 cm^3 of ethylene are introduced, almost no reaction is detected after 20 hr. This test shows that alumina is not itself catalytically active, because otherwise it should conserve some of its activity during the second test. A reasonable hypothesis is that the adsorbed hydrogen, required for the reaction, is in part consumed during the first test and in part removed during the flushing by hydrogen gas.

Indeed, if after the standard activation procedure alumina is flushed by hydrogen during 1 hr at 110°C, only 17 cm^3 of ethane are formed in about 20 hr, instead of 45 cm^3. Again, the migration of nickel from the catalyst to alumina cannot be incriminated, because flushing by hydrogen would not change the activity of nickel.

It was also pointed out previously that the amount of hydrogen fixed per 1 g of alumina is 1.3 cm^3 at 110°C and 0.5 cm^3 at 25°C. If after the standard activation procedure alumina is cooled to 25°C and again reheated to 110°C, only 16.6 cm^3 of ethane are formed in about 20 hr instead of 45 cm^3 for alumina maintained at 110°C. These results show that a correlation must exist between the amount of hydrogen fixed on alumina and the catalytic activity. They also show that migration of nickel from the catalyst to alumina cannot be responsible for the reaction which would proceed to the same extent (at 110°C) with or without intermediate cooling of alumina to 25°C.

Finally, the amount of hydrogen fixed on alumina at 110°C (1.3 cm^3) is not directly linked with the amount of ethane formed (45 cm^3). For a simple addition of this hydrogen to ethylene only 1.3 cm^3 of ethane, at most, would be formed if the catalytic effect was not correlated with the hydrogen from the gas phase.

In order to check if a simple addition of adsorbed hydrogen to ethylene is possible, the following test was performed. After a standard activation procedure hydrogen was flushed at 110°C with helium or with nitrogen during 1 hr and then only ethylene was introduced. No reaction took place for both conditions, showing that the fraction of remaining hydrogen (considered as comparable to that remaining after flushing by hydrogen) cannot be simply added to ethylene (the limit of the detection of ethane being of the order of 10^{-4} cm^3). Clearly, molecular hydrogen is also required for the hydrogenation of ethylene on alumina with spilt-over hydrogen.

4. *Influence of the Nature of Alumina*

Alumina aerogel used in the previous experiments is amorphous (*7*) and the question arises as to whether the hydrogen spillover is limited to this type of material. Therefore, in a new series of experiments, crystallized, nonporous, delta-alumina (Degussa P110) was used. It was shown previously (*4*) that this oxide is a conventional catalyst for the hydrogenation of ethylene above 400°C. The activation treatment of delta-alumina was performed in the reactor of Fig. 1, with the nickel-on-alumina aerogel catalyst, as before, during 14 hr under 760 Torr of hydrogen at 300°C, 8 hr at 110°C and 1 hr at 25°C. The catalyst was then withdrawn and isolated and 50 cm^3 of ethylene were introduced. No detectable quantity of ethane was formed at 25°C after 20 hr, but when the temperature was raised to 110°C, 17 cm^3 of ethane were formed after 20 hr. This amount is practically the same as that found on alumina aerogel after the comparable activation treatment (Table 1). It may be concluded that activation in hydrogen in the presence of nickel catalyst has a more general significance (it is also shown below that a platinum catalyst may be used instead of nickel) and that the amorphous nature of alumina initially employed is not responsible for the effect observed, because crystalline (delta) alumina behaves in a similar way. The determination of the nickel content in the delta-alumina by atomic absorption spectroscopy gave a value of 19 ppm for the initial delta-alumina sample and 14 ppm after the experiment of hydrogenation of ethylene.

In a final experiment the catalyst in the pan A of Fig. 1 was not covered by delta-alumina in the holder D, but simply hung at some distance (a few millimeters) from the top of the alumina powder during the standard activation procedure (without cooling to 25°C).

No reaction took place with ethylene at 110°C once the catalyst was removed and isolated. This experiment shows that (i) hydrogen cannot spill over through the gas phase but only through the adsorbed phase (when the catalyst is in contact with alumina), (ii) any migration of nickel from the catalyst to alumina through and eventual formation of a volatile nickel compound must be discarded. Indeed, in this case it would be immaterial to have the catalyst distant from alumina or in contact with it if nickel can migrate to alumina (or to the walls of the reactor) through the gas phase.

In the first qualitative series of experiments, reported previously (*1*), catalytic activity in the hydrogenation of ethylene was observed already at 25°C, whereas, in the present series a noticeable activity is recorded at 110°C (Table 1). The alumina aerogel which was used in the first series, examined by ir absorption spectroscopy, gave no evidence of the presence of methoxy groups; whereas the alumina aerogel samples used in the present work contain these groups, which are formed during the heating of alumina gel in methanol in the autoclave (*7*). Also, in order to check if methoxy groups hinder the hydrogenation of ethylene at 25°C after the hydrogen activation treatment in the presence of the catalyst, alumina aerogel was demethoxylated by water vapor carried in an oxygen stream at 280°C. After an evacuation at 350°C during 12 hr the demethoxylated alumina was activated, with the catalyst, in hydrogen at 300°C (16 hr), 110°C (8 hr) and 25°C (2 hr). The catalyst was then removed and isolated and 50 cm^3 of ethylene were introduced. The reaction at 25°C was then recorded and showed a greater rate than for the methoxylated alumina (Table 1). Indeed, after 24 hr or reaction 0.6 cm^3 of ethane are formed. After 850 hr almost one half of the initial amount of ethylene was converted into ethane. Figure 3 shows the kinetics of the reaction. The induction period is well observed, as previously for methyoxylated alumina at 110°C (sample M, Table 2 and Fig. 2). This induction period is again observed at 25°C or at 110°C when delta-alumina is used after activation in the presence of platinum on amorphous alumina. This type of kinetics is not observed for hydrogenation of ethylene on metal catalysts (*8,9*). Neither is it observed on sample L (blank) in Fig. 2 (note the discontinuity of the ordinate). The room temperature activity of demethoxylated alumina may be due either to the removal of methoxy groups or to the hydroxylation of the surface of alumina during the demethoxylation treatment. This problem needs more extensive study.

5. *Infrared Absorption Evidence for Hydrogen Spillover on Alumina*

The amorphous alumina aerogel, compressed in the form of a pellet, was examined by ir absorption spectroscopy (Beckman I.R.4) after evacuation (10^{-6} Torr) at 350°C during 14 hr and cooling to 25°C. Figure 4 shows the spectrum obtained (No. 1). The large band at 2700–3700 cm^{-1} is due to the stretching vibration of OH groups of alumina together with that of –CH groups, whereas bands at 1610 and 1493 cm^{-1} are probably due to the deformation vibration of hydroxyls in water or rather to carbonaceous impurities (*7*). These bands are consistent with the presence of methoxy groups in the alumina aerogel.

If the alumina pellet is heated at 300°C during 14 hr under 760 Torr of hydrogen and then cooled to 25°C the same spectrum is again recorded. But if the pellet made from the nickel-on-alumina aerogel catalyst is joined together with the alumina pellet in the ir cell and submitted to the same hydrogen treatment, the spectrum recorded after removal of the catalyst pellet, without exposure of the cell to air, shown in Fig. 4 (No. 2), exhibits four additional bands at 1300, 1340, 3000 and 3077 cm^{-1}. These bands disappear after evacuation of the pellet at room temperature (Fig. 4, spectrum 1) and may be due either to hydrogen spillover on alumina or to a modification on alumina surface by hydrogen (and in the presence of the catalyst). They cannot be due to C–H frequencies associated with unsaturated structures because these contaminants should be observed for the alumina pellet, previous to

FIG. 4. Infrared spectra of alumina with spilt-over hydrogen or deuterium.

contact with the nickel catalyst, both in vacuum and in hydrogen. Figure 4, spectrum 1, shows that this is not the case. Moreover, a simple evacuation at room temperature of the system exhibiting the spectrum 2 would not remove these unsaturated -CH bands. However, the evacuation brings back the spectrum 1. The same spectrum (No. 1) is also observed if the alumina pellet is joined together with nickel on alumina aerogel catalyst in the ir cell, in vacuum, instead of under hydrogen. The first hypothesis is confirmed by the deuterium isotopic shift observed when the alumina and the catalyst pellets are submitted to deuterium at 300°C for 14 hr and cooled to 25°C. The spectrum registered (Fig. 4, No. 3) shows that the bands, previously at 3077 and 3000 cm^{-1}, are now at 2390 and 2260 cm^{-1}, whereas bands at 1340 and 1300 cm^{-1} disappear from the scanned region. The band at 2900 cm^{-1} which is now revealed and which in spectrum 1 was scarcely apparent, is probably due to carbon residues in the alumina aerogel (7). Since by evacuation at 25°C the disappearance of the band at 2260 cm^{-1} proceeds at a higher rate than that of the band at 2390 cm^{-1}, these bands cannot therefore have originated from a single species. However, both are shifted by deuterium by a constant factor (0.76) that is close to the theoretical value for the isotope shift. This provides good evidence that the original absorption was due to vibrations of surface species formed by hydrogen spillover. The new bands formed by hydrogen or deuterium spillover (Fig. 4, spectra 2 and 3) are very sharp and are not consistent with OH groups interacting strongly with neighboring groups (responsible for broad bands at 3000 (OH) or 2300 cm^{-1} (OD) region]. The spilt-over hydrogen is therefore only weakly bound to the surface as is also demonstrated by the vanishing of these sharp bands after evacuation at room temperature.

Hydrogen can be linked directly to the cation as in ZnO (*10*) but in the case of alumina the Al–H bond would exhibit an absorption band in the region of 1800 cm^{-1} (*11,12*) which is distant from the four bands registered after the spillover of hydrogen. A tentative assignment of bands at 3077 and 3000 cm^{-1} would link these bands with the OH stretching frequency (*13,14*) and the bands at 1340 and 1300 cm^{-1} with the bending frequency. The two types of adsorption sites for spilt-over hydrogen would correspond to oxygen ions linked either with aluminium or with hydrogen (hydroxyl groups).

6. *The Mechanism of the Reaction*

Because there is no direct correlation between the amount of hydrogen fixed on alumina (1.3 cm^3 at 110°C) and the amount of ethylene converted into ethane (45 cm^3 out of 50 cm^3 after 20 hr at 110°C) and also because of the simultaneous need for adsorbed (spilt-over) hydrogen and molecular hydrogen in order to hydrogenate ethylene, a chain reaction in the adsorbed phase may be envisaged (*15*). The following experiments give some weight to this hypothesis.

After the standard activation procedure of the alumina aerogel, 50 cm^3 of ethylene were introduced at 110°C and the reaction, monitored for 0.5 hr, corresponded to the formation of 0.1 cm^3 of ethane. Then, 0.5 cm^3 of nitric oxide (NO) were introduced into the reaction mixture. After 24 hr of reaction only 0.2 cm^3 of ethane were formed instead of 45 cm^3 or more as previously in the absence of NO which is well known as a chain reaction inhibitor. The corresponding mechanism could therefore be (*13*):

$$H_{2(g/Ni)} \rightarrow 2H_{(ads/alumina)} \qquad \text{initiation,}$$

$$\left.\begin{aligned} &C_2H_{4(ads\ or\ g)} + H_{(ads)} \rightarrow \\ &\quad C_2H_{5(ads)} \\ &C_2H_{5(ads)} + H_{2(g)} \rightarrow \\ &\quad C_2H_{6(g)} + H_{(ads)} \end{aligned}\right\} \qquad \text{propagation,}$$

$$C_2H_{5(ads)} + H_{(ads)} \rightarrow C_2H_{6(g)} \qquad \text{termination.}$$

These equations imply the presence of adsorbed C_2H_5 radicals which would not be firmly bound to the alumina surface. Their migration on the surface at 110°C would be possible. An attempt to find these radicals through the formation of a mirror of zinc (Paneth type) failed but gave complementary arguments in favor of a chain reaction. As the radicals eventually formed are in the adsorbed phase, a mixture of zinc powder and of alumina aerogel was made and after evacuation at 320°C it was submitted to the standard activation procedure in hydrogen, in the presence of nickel-on-alumina aerogel catalyst in the reactor of Fig. 1. After removal and isolation of the catalyst, 50 cm^3 of ethylene were entirely hydrogenated into ethane in 4 hr at 110°C. During this reaction one part of the external tubing of the reactor of Fig. 1 was heated to 450°C, in order to decompose, with formation of a mirror, the diethylzinc eventually formed on the catalyst. No zinc mirror was, however, observed. The diethylzinc could react with OH surface groups to liberate ethane and form Al–O–Zn structures. But the high activity of zinc–alumina mixture may be due to some other effect than the spillover of hydrogen and the chain reaction. Also, in a second experiment this mixture was treated with hydrogen at 300 and 110°C but without the catalyst. The same activity in the hydrogenation of ethylene at 110°C was again recorded and no zinc mirror was formed. But nitric oxide injected into the reaction mixture does not show any inhibiting effect. This behavior tends to indicate that hydrogenation of ethylene on zinc–alumina mixture is a conventional associative reaction and not a chain reaction. As neither the zinc powder alone, nor the alumina alone, treated in hydrogen at 300°C and then at 110°C, in the absence of the catalyst, are active in the hydrogenation of ethylene at 110°C it is probable that in the zinc–alumina mixture some ZnO is formed on zinc, by reduction on alumina aerogel. Zinc oxide is a well-known conventional catalyst in the hydrogenation of ethylene (*16*). The dielectric loss observed in an ESR cavity for a zinc–alumina mixture heated in hydrogen at 300°C is in agreement with the hypothesis of ZnO formation. Finally, the hydrogenation of ethylene at 300°C in the presence of alumina aerogel, which is then a conventional reaction (Table 2), as well as in the presence of nickel-on-alumina aerogel catalyst at 110°C, is not inhibited by nitric oxide. Therefore zinc oxide on zinc at 110°C, nickel-on-alumina aerogel at 110°C and alumina aerogel at 300°C are conventional catalysts for an associative type reaction, whereas the hydrogenation of ethylene at 110°C on alumina containing spilt-over hydrogen, which is inhibited by NO, could be a radical type chain reaction. A paramagnetic species, other than atomic hydrogen, was indeed observed by ESR (10^{15} spins/g Al_2O_3) during the reaction at 110°C of ethylene with hydrogen spilt-over on alumina (*17*). The identification of this species, tentatively assigned to ethyl radical, will be described in a forthcoming paper.

Experiments on hydrogen spillover from $Pt–Al_2O_3$ catalyst to alumina (to be reported in a forthcoming paper) do not show any inhibiting effect of NO on the hydrogenation of ethylene. Simultaneously other characteristics are also modified for this system. For example, the evacuation of hydrogen from alumina, after the activation procedure which requires here a temperature of 400°C, does not inhibit the hydrogenation of ethylene, which is opposite to that found in the $Ni–Al_2O_3$ system (see above). It would then follow that NO does not act on $Ni–Al_2O_3$ system simply as a poison (it would also poison the $Pt–Al_2O_3$ system) and that the hydrogenation of ethylene results from two different mechanisms on the two systems. If the associative type conventional reaction, insensitive to NO, takes place on the $Pt–Al_2O_3$ system (as for nickel on alumina catalyst, zinc oxide on zinc, and pure alumina at 300°C) the chain reaction, which is arrested by NO, seems probable on the $Ni–Al_2O_3$ system.

In conclusion, it is considered that hydrogen spillover from nickel catalyst to alumina, through the adsorbed phase, is responsible for the catalytic activity of alumina in the hydrogenation of ethylene at 25°C or at 110°C. This hydrogen is easily removed by evacuation, as shown by ir spectroscopy. Simultaneously catalytic activity disappears. The hydrogenation of ethylene with the spilt-over hydrogen and molecular hydrogen seems to be a chain reaction (with radicals in the adsorbed phase). But this reaction is not restricted to amorphous alumina aerogel, with methoxy groups, as it is also observed on demethoxylated aerogel and on crystallized delta-alumina.

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