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Catalytic and Infrared Demonstrations of the Effect of Hydrogen Spillover on a Gel of Silica

It has been shown previously that pure alumina can be transformed into a hydrogenation and isomerization catalyst, active at fairly low temperatures, after a particular treatment involving hydrogen spillover from nickel or platinum catalysts (*1*, *2*). As silica is also very often used as a catalyst carrier, an attempt at its activation by the same method (*1*, *2*) is of interest. Because alumina aerogels were found to be more easily activated by hydrogen toward catalytic reaction (*2*) than alumina xerogels or aerosols, the silica was also investigated in the form of aerogel.

A silica aerogel was prepared by hydrolysis of tetramethoxysilane in methanol which was then evacuated in an autoclave under hypercritical conditions (*3*). The surface of this aerogel was covered by $O-CH_3$ groups but these may be easily converted into OH groups by heating the aerogel in air at 430°C for 48 hr. Both types of surface have the same behavior with respect to the properties described below and most of the experiments were performed with the methoxylated aerogel of surface area 900 m^2 g^{-1} which would correspond to a particle size of 30 Å.

The procedure for activating silica aerogel by hydrogen spillover was the same as that already described for alumina (*1*, *2*), i.e., physical contact between 10 and 20 mg of a Pt/Al_2O_3 catalyst contained in a bucket and the batch of 1 g silica aerogel to be activated; raising the temperature from 25 to 430°C under reduced pressure (10^{-5} Torr) and maintaining this temperature for 8 hr; treatment in hydrogen (1 atm) for 12 hr at 430°C. The temperature was then lowered to the selected reaction temperature (200°C in the case of the hydrogenation of ethylene, or 170°C in the case of benzene (*4*), 1-3: or 1-4:cyclohexadiene, or cyclohexene). The bucket containing the Pt/Al_2O_3 catalyst (and a small amount of silica) was removed and isolated from the reactor and the second reactant (ethylene, 50 cm^3; benzene, 10 cm^3; cyclohexadiene, 10 cm^3; or cyclohexene, 10 cm^3) was introduced. The batch reactor (with recirculation of gases), 1 liter in volume, contained therefore only the activated silica aerogel ($\sim$1 g). The gases were analyzed by gas chromatography using a flame ionization detector during the activation procedure at 430°C, as well as during the hydrogenation reaction at 170 to 200°C. The Pt/Al_2O_3 catalyst was prepared by impregnation with chloroplatinic acid of an amorphous alumina aerogel (S = 500 m^2 g^{-1}) and its platinum content was 0.6%. The dispersion of the metal, determined by hydrogen chemisorption, was 44%.

A. Catalytic Behavior

Blank tests on fresh samples of silica aerogel were performed in two different conditions. In one run, the activation procedure was performed in the absence of the Pt/Al_2O_3 catalyst. One gram of silica aerogel was evacuated at 430°C for 8 hr and then 1 atm of H_2 was introduced and allowed to remain for 12 hr. The tempera-

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ture was than lowered to 200°C and ethylene (50 cm^3) was introduced into the reactor. No reaction took place even after 24 hr of contact. It is concluded that vacuum and hydrogen treatment at 430°C, in the absence of Pt/Al_2O_3 catalyst, is not able to create on silica sites active for the hydrogenation of ethylene. In the second run, 1 g of fresh silica aerogel was maintained in contact with the Pt/Al_2O_3 catalyst in the removable bucket. This system was evacuated at 430°C for 8 hr; then helium (instead of hydrogen) under 1 atm was introduced and allowed to remain for 12 hr. After cooling the reactor to 200°C the bucket containing the metal catalyst was removed and isolated as in a normal procedure; the gas phase (helium) was evacuated from the reactor and a mixture of hydrogen (~1000 cm^3) and ethylene (50 cm^3) under a total pressure of 1 atm was introduced. Again no reaction took place even after 24 hr of contact. This blank shows, on the one hand, that no migration of platinum onto silica occurred during the activation period and, on the other hand, that hydrogen was necessary to activate silica but not in the molecular form (see the first blank). There are probably hydrogen atoms adsorbed on platinum particles which migrate from the metal and create the catalytic active sites on silica (*1*, *2*, *4*, *5*). The GC analysis of the gas phase during the normal activation treatment at 430°C showed the presence of methane. No methane was found under similar conditions but in the absence of Pt/Al_2O_3 catalyst or in the atmosphere of helium (instead of hydrogen) in the presence of the catalyst. It seems obvious that hydrogen spilled over from the metal (Pt) through the support (Al_2O_3) onto the silica aerogel is able to break the C–O bond of the surface methoxy groups giving CH_4 (and –OH surface species as shown below).

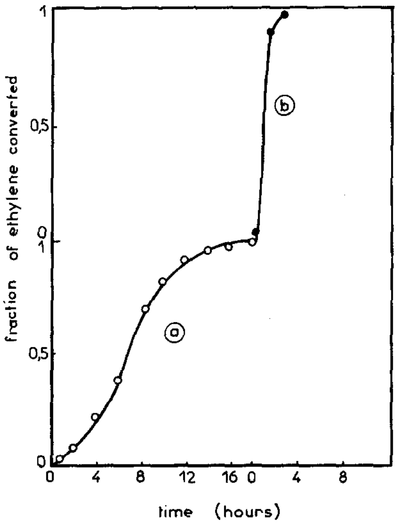

Fig. 1. Conversion of ethylene into ethane at 200°C on an activated silica aerogel. (a) First run, (b) second consecutive run.

The amount of hydrogen taken up by silica in the normal activation treatment was determined between 430 and 200°C by conventional adsorption measurements on silica admixed with 20 mg of Pt/Al_2O_3 catalyst, by subtracting the amount of hydrogen adsorbed by pure catalyst. It was of the order of 1.4 cm^3 of H_2 per gram of silica at 200°C. Pure silica (without admixed Pt/Al_2O_3 catalyst) showed no adsorption in the same conditions. The number of sites on the silica surface accepting the spilled over hydrogen was estimated to be of the order of $10^{12}/cm^2$.

Figure 1 (curve a) shows the results of the hydrogenation of the first dose (50 cm^3) of ethylene into ethane at 200°C over about 1 g of activated silica aerogel. The induction period is to be noted, whereas for the second dose (50 cm^3, curve b) and following doses (not shown) the reaction is faster and does not exhibit the induction period. This retardation effect is due to the spilled over hydrogen (exhausted after the first dose run). Indeed, if prior to the reaction with ethylene the fresh activated silica is first evacuated at 200°C or exposed to air between 25 and 400°C and again evacuated at these temperatures, the subsequent introduction of the H_2–C_2H_4 mixture at 200°C gives the type b curve of Fig. 1, without the induction period. It thus appears that the catalytic activity of silica is not related to the amount of spilled over hydrogen (1.4 $cm^3\ g^{-1}\ SiO_2$) but is reproducible for many doses (50 cm^3 each) of ethylene which are hydrogenated by hydrogen present in the gas phase. The introduction of ammonia is without any effect on this reaction.

If the spilled over hydrogen is evacuated from a fresh activated silica and then hydrogen (~1000 cm^3) and benzene (10 cm^3) under 1 atm are introduced at 170°C, only ethane is found (~10 cm^3) after the reaction is accomplished, but a transient formation of acetylene is recorded. Benzene in the presence of helium (instead of hydrogen) is converted to acetylene only. If the spilled over hydrogen is not evacuated prior to the reaction, benzene is again converted to ethane, but small amounts of cyclohexane and cyclohexene, corresponding to the amount of the spilled over hydrogen (1.4 $cm^3\ g^{-1}\ SiO_2$), are also found. The hydrogenation of benzene into ethane is therefore a catalytic reaction involving molecular H_2, whereas the formation of cyclohexene and cyclohexane implies the addition to benzene of the spilled over hydrogen. The first reaction is poisoned by ammonia, whereas the addition of the spilled over hydrogen to benzene giving cyclohexene (but not cyclohexane) is insensitive to ammonia.

If after the standard activation procedure cyclohexene is used at 170°C as the reagent (instead of benzene), only cyclohexane is found in an amount corresponding to the exhaustion of the spilled over hydrogen. If the spilled over hydrogen is evacuated prior to introduction of the mixture of hydrogen and cyclohexene, no transformation of this reagent is recorded.

1-3:Cyclohexadiene behaves at 170°C as benzene giving ethane, and acetylene as a transient. In the same way it gives acetylene in the presence of helium. But 1-4:cyclohexadiene at 170°C is converted only into acetylene, in the presence of both hydrogen and helium. The conversion of these aromatic hydrocarbons is poisoned by ammonia or by a previous treatment in air, but the hydrogenation of acetylene into ethane (as previously the hydrogenation of ethylene) is insensitive to ammonia or to air.

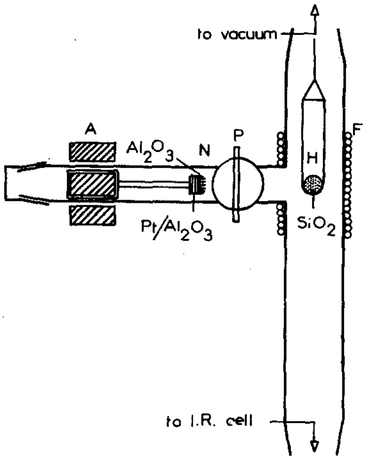

FIG. 2. Experimental setup for the activation of silica by Pt/Al_2O_3 catalyst prior to the ir absorption measurement.

It would therefore appear that a permanent catalytic activity of an unconventional type is conferred on silica by the hydrogen spillover activation procedure. The spilled over hydrogen leads to a different behavior of the system but only a very limited one which may be suppressed by the evacuation of the spilled over hydrogen prior to the reaction.

B. Infrared Evidence

A special type of ir cell has been used to reproduce, in the ir spectrometer, the experimental conditions for the activation of silica, mentioned previously (Fig. 2). A pellet of Pt/Al_2O_3 catalyst (the same as that used before) was placed in a horizontal, removable (by a magnet) sample holder N, and covered by a 3-mm-thick layer of compressed δ-alumina nonporous aerosol

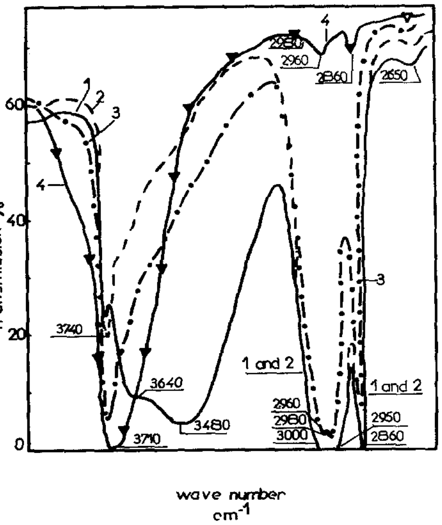

FIG. 3. Infrared spectra at 25°C of: (1) nonactivated silica aerogel under vacuum, (2) same sample but in the presence of H_2 at 430°C, (3) silica aerogel activation by the spillover, (4) nonactivated silica in the presence of O_2 at 430°C.

in order to prevent any loss of particles of catalyst. The spilled over hydrogen must therefore diffuse through this compressed alumina layer before it can reach the silica in the form of a compressed disk which is placed in the holder H. The silica disk could be either raised in the heating section F or lowered in the head (at 25°C) of the ir cell (*6*). The contact between the two surfaces during the activation procedure was rather loose and was only determined by the mechanical strength of the silica disk. The Pt/Al_2O_3 sample holder could be isolated from the rest of the cell through the stopcock P.

The evacuation of the silica disk at 25°C for 8 hr at 10^{-5} Torr leads to curve 1 of Fig. 3 which shows the presence of ir bands characteristic of free and linked –OH groups at respectively 3740 and 3640 to 3480 cm^{-1} and the presence of strong bands due to the methoxy groups at 2980 and 2860 cm^{-1}. These bands were not entirely recorded because the transmission of the sample fell to zero before the maximum of the absorption band appeared. After this recording the silica disk was evacuated (10^{-5} Torr) at 430°C for 12 hr in part F (Fig. 2) and curve 2 of Fig. 3 was then recorded (at 25°C) showing a sharp decrease of the bands due to linked –OH groups and the appearance of a strong free –OH absorption band at 3740 cm^{-1}. The bands due to $-OCH_3$ groups remained unmodified. A subsequent treatment in hydrogen (1 atm) at 430°C for 12 hr did not change the spectrum. All these treatments corresponded to the blank run, without the Pt/Al_2O_3 catalyst, described previously. Similarly, the subsequent introduction of ethylene into the ir cell (4–6 Torr), the silica disk being heated to 200°C by the oven F, did not show any ethane in the gas phase (no band at 3010 cm^{-1}) even after 12 hr of contact.

In a second type of run, the Pt/Al_2O_3 pellet was allowed to contact the silica disk during the H_2 treatment at 430°C for 12 hr. The ir spectrum then registered (curve 3, Fig. 3) shows an increase of the band of the free –OH species at 3740 cm^{-1} and a noticeable decrease of the bands due to the methoxy group (at 2980 and 2860 cm^{-1}) by comparison with curve 2 of Fig. 3. Once the catalyst was removed and isolated by the stopcock P, the silica was able at 200°C to convert ethylene which was introduced (4–6 Torr) into ethane. Indeed, the band at 3100 cm^{-1} of ethylene disappeared and bands of ethane at 3010 cm^{-1} and of the C–H bond at 2950 cm^{-1} appeared. When the silica disk was treated at 430°C with 300 Torr of O_2 (instead of H_2) in the presence of the Pt/Al_2O_3 catalyst during 12 hr, the recorded spectrum (Fig. 3, curve 4) showed a strong decrease of the $-OCH_3$ absorption bands and a large increase of the band due to the free –OH species. Simultaneously CO_2 was detected in the gas phase. It does not seem that oxygen spillover, from platinum to silica, is required to destroy the methoxy groups, because the same results are also obtained in oxygen at 430°C but without the Pt/

Al_2O_3 catalyst. After the evacuation of oxygen and isolation of Pt/Al_2O_3 catalyst no hydrogenation of ethylene with C_2H_4–H_2 mixture was observed at 200°C. But the same silica disk, after a contact with Pt/Al_2O_3 catalyst in hydrogen at 430°C, was active in ethylene hydrogenation and presented an absorption spectrum identical to spectrum 4 of Fig. 3. The oxygen treatment is unable to activate the silica aerogel toward the hydrogenation of ethylene at 200°C and shows also that no migration of platinum to the silica disk occurred through the intermediate alumina layer. But the silica aerogel which is then cleaned from methoxy groups becomes again active in hydrogenation of ethylene after activation by hydrogen spillover.

These experiments demonstrate that in the activation procedure of silica aerogel by hydrogen in the presence of Pt/Al_2O_3 catalyst, the surface of silica is modified by the spilled over hydrogen in such a way as to create sites for the hydrogenation of ethylene at 200°C. This spilled over hydrogen simultaneously demethylates partially the surface of the aerogel which becomes instead hydroxylated.

In conclusion, it seems that hydrogen spillover can convert a refractory oxide such as silica into a catalyst for the hydrogenation of ethylene and for some unconventional reactions with benzene, cyclohexadienes, and cyclohexene. The spilled over hydrogen is rather an inhibitor of the hydrogenation of ethylene and gives an addition reaction (noncatalytic) with benzene and cyclohexene (and probably cyclohexadienes). This reaction is noncatalytic in the absence of Pt/Al_2O_3 catalyst, because the spilled over hydrogen is exhausted by the reaction. However, it is possible that in the presence of a conventional hydrogenation catalyst (metal on support), the spilled over hydrogen being continuously supplied, the conversion of benzene into cyclohexane is due to this type of hydrogen.

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