JOURNAL OF CATALYSIS **112**, 116–125 (1988)

Hydrogen Spillover on Silica

II. Kinetics and Mechanism of the Induction of Catalytic Activity

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Received October 17, 1986; revised February 15, 1988

To understand the potential significance of the phenomena associated with hydrogen spillover it is necessary to understand the mechanism by which catalytic activity is induced onto oxides and the relative activity of these sites. To quantify the relative activity, it is necessary to estimate the number of active sites that are created so that a "proper" turnover frequency can be calculated. We have studied the hydrogenation activity induced on silica by hydrogen spilled over from platinum as a function the pretreatment of the silica and the time and temperature of exposure to spiltover hydrogen. The induction of activity requires long periods of exposure (>6 h, increasing to 12 h) at high temperatures (400–460°C). With the optimum conditions the concentration of active sites approaches $10^{13}/cm^2$ of silica surface and the maximum turnover frequency of the created sites is estimated as $10^{-1}\ s^{-1}$ for ethylene hydrogenation at 200°C. The catalytic sites seem to be created from the reaction of specific "associated" (vicinal or geminal) hydroxyls on the silica with spiltover hydrogen. © 1988 Academic Press, Inc.

INTRODUCTION

The purpose of this research study is to establish a quantitative basis on which to compare the catalytic activity induced by hydrogen spillover. To establish this basis it is necessary to determine the concentration of active sites and thereby to estimate the turnover frequencies (molecules reacted per active site per second), TOFs, of the activated surface. The hydrogenation of ethylene over silica was studied because silica is not a catalyst for this reaction without activation by spiltover hydrogen and because the reaction is reasonably well understood on metallic and oxide surfaces. Furthermore, the activity induced onto the silica is sensitive to the conditions of pretreatment and exposure to spiltover hydrogen. Also the reaction is catalytic as numerous turnovers (based on the highest estimates for the number of active sites) have been measured without evidence of deactivation (*1*).

The pretreatment conditions commonly affect catalytic activity. These conditions include the time and temperature of calcination or evacuation, and the pressure and temperature at which the catalyst may be activated (e.g., by exposure to spiltover hydrogen). From MacBain TPD and TPR studies (*1*) and prior studies by Peri (*2*), Hair and Hertl (*3*), and Kiselev and Lygrin (*4*), it is apparent that the time and temperature of the pretreatment under vacuum control the hydroxyl population on silica. Subsequent to evacuation the silica can be exposed to hydrogen spilled over from a metal (e.g., Pt) for different times and temperatures. To investigate the potential influences of these activation conditions it is first necessary to understand the nature of the activity that is induced on oxides by spiltover hydrogen.

Spiltover hydrogen has been found to react with oxides in a variety of ways. In the mildest process it can exchange with surface hydroxyls or demethoxylate a methoxylated surface (forming methane). It can be involved in the bulk reduction of oxides to bronzes which may involve the incorporation of the hydrogen into the crystalline structure. Spiltover hydrogen has been found to both inhibit and induce catalytic

0021-9517/88 $3.00

activity on nonmetallic surfaces. These phenomena have been recently reviewed (*5*) and were discussed in our first paper in this series (*6*).

As a result of hydrogen spillover at high temperatures for long periods of time, oxides have been found to be active for the hydrogenation of ethylene (*6–8*) and benzene (*9, 10*). The nature of the induced activity depends on the nature of the oxide being activated as well as on the pretreatment conditions.

It is desirable to separate three phenomena: the reaction of hydrogen on an adsorbing metal, the reaction of spiltover hydrogen on an oxide surface, and the catalytic activity induced by spiltover hydrogen on the oxide. Teichner *et al.* have developed a reactor to separate the reactions on the metal (the source of spillover) from the activity induced on the metal oxide, the acceptor of the spiltover hydrogen (*11*). A similar design was employed in these studies.

Recently Teichner *et al.* summarized their studies concerning the activation of alumina, silica, or magnesia by hydrogen or oxygen spillover (*12*). They concluded that these oxides can be activated by hydrogen spillover at 700°K for catalytic reasons in the 320 to 540°K temperature range. The spiltover hydrogen reacts only indirectly, being consumed by reaction with the first dose of reactant (e.g., ethylene or benzene). The spiltover hydrogen can be evacuated prior to the reaction. The sites that are created are capable of cracking and dehydrogenation reactions in the absence of molecular or spiltover hydrogen. At least two, and possibly three, types of sites have been inferred for each oxide.

On activated silica gel (*13*), one type of site seems active for the hydrogenation of ethylene or acetylene. These sites are insensitive to ammonia, air (O_2), or 1-3-cyclohexadiene at 700°K. However, 1-4-cyclohexadiene poisons the hydrogenation of acetylene but not the hydrogenation of ethylene. This leads the authors to conclude that there are two types of sites created. Moreover, exposure of the activated silica to air or ammonia poisons the cracking or cyclization reactions (a third type of site . . . ?). Demitriev *et al.* (*14*) proposed that spiltover hydrogen could remove oxygen ions from the silica surface leaving an unscreened silicon (Si^+ or Si^{2+}) which would react as Lewis acid sites and be poisoned by NH_3 or O_2.

For all of the oxides that have been studied the concentration of sites accepting the spiltover hydrogen (and thus possibly the concentration of active sites created) is consistently estimated to be around $10^{12}/cm^2$. These concentrations were calculated by volumetric studies of hydrogen adsorption (*15–17*), by titration with ethylene (*6*) or pentene (*18*), by TPD (*8*) and by NMR (*19*) techniques. Does this concentration of adsorbed, spiltover hydrogen correspond (1 : 1) with the active sites that are created? This has been suggested in several earlier studies.

Catalysts often require a sequence of pretreatment steps to achieve optimum activity. Calcination and/or evacuation are often employed (to remove surface contaminants, e.g., hydrocarbons or water). At the same time the surface may be partially or totally dehydroxylated. The catalyst may be exposed to oxidizing and/or reducing conditions to modify the surface chemistry or again remove contaminating adsorbents.

Maret *et al.* have described a standard spillover activation procedure to induce activity on "inert" irreducible oxides, such as silica or alumina (*20*). Three steps are involved: evacuation at 700°K at $<10^{-5}$ Torr for 17 h; exposure to 700 Torr of hydrogen spiltover at 700°K for over 6 h; cooling the catalyst to reaction temperature in hydrogen. The Pt/Al_2O_3 source of spillover was present during these processes but was removed and isolated prior to the reaction.

EXPERIMENTAL

As mentioned above, the reactor used in these studies is a modification of the basic design of Teichner *et al.* (*11*) and is de-

TABLE 1

Representative Activation Conditions for Aerosil, A-200

Experiment	Evacuation		Activation (exposure to spiltover hydrogen)		
	Temp. (°C)	Time (h)	H_2 (Torr)	Temp. (°C)	Time (h)
1	430	7	192	430	3
2	422	8	241	428	10
3	423	8	221	425	14
4	424	8	380	435	8
5	430	8	197	400	14
6	430	8	216	460	10
7	430	8	274	435	6
7A	430	8	238	434	8
8	440	8	286	400	10.5
9	428	12	326	430	24
10	430	12	192	430	12
11	430	12	200	430	8
12	430	12	163	423	10
13	500	12	182	430	11.5
14	475	17	425	475	23
15	440	21	214	437	22
16	405	23.5	156	396	22.5

scribed in the first paper of this series (*6*). The major difference in our reactor is that the contact between the Pt source of spillover and the SiO_2 accepting surface is only indirect; i.e., there is a fritted glass bucket through which the spiltover hydrogen must diffuse from source to accepting surface. An all-glass system was used employing a three-stage diffusion pumping system (capable of evacuation to 10^{-9} Torr). Convalex diffusion oil was used in the diffusion pump as was Apiezon T (or DOW silica grease to reduce hydrocarbon impurities) in the stopcocks (vapor pressures $<10^{-10}$ Torr). Teichner has found that the induction of activity is not changed in any manner if a "greaseless" system is used, i.e., with glass/metal-bellow valves replacing stopcocks (*20*).

Compared to the "standard activation procedure" as outlined by Maret *et al.* (*20*), each of the parameters involved in the process of the activation of silica was studied in varying degrees. These parameters include the time and temperature of evacuation and the time, temperature, and pressure of exposure to spiltover hydrogen. We used alumina-supported platinum as the source of spillover and Degussa Aerosils as the accepting silica substrate. Table 1 shows representative conditions used in the activation procedures for the Degussa Aerosil, A-200; 0.04% Pt/Al_2O_3 provided by UOP was the source of spillover except experiment 9 (which used Pt/SiO_2).

The Degussa Aerosil used in these studies is one of the highest purity silicas commercially available. Degussa claims the following nonsilica, nonalumina impurities; i.e., Fe and Cr are the major impurities but are typically less than 1 ppm and all other metals total less than 1 ppm.

Using atomic adsorption on samples following our "standard" activation procedure or after reaction, we find *no detectable Fe, Cr, or Ni.* The sensitivity limit of the technique employed is >3 ppm. The absolute maximum for any of these metals would be <3 ppm, in line with Degussa's claims. Note that Teichner has used neutron activation to determine that Pt does not migrate onto the silica with this type of reactor and activation procedure (*21*). We therefore conclude that metal impurities are not the source of the catalytic activity that is found.[1]

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[1] Without surface enrichment, the level of surface impurities (for Ni, Fe, or Cr, for example) would have to be greater than 10^4 ppm to give 10^{12} sites per square centimeter of surface. If impurities at lower than $10^{12}/\text{cm}^2$ were the source of activity, their corresponding TOFs would need to be greater to give evidence for the observed activity. At $10^{10}/\text{cm}^2$, for example, the TOF would exceed 10/s (note the estimates in the first paper of this series were up to 10^{-1}/s for $10^{12}/\text{cm}^2$ sites (*6*)). Part per million levels of impurities could give rise only to small concentrations of surface impurity sites. These sites would have to be very active (far more than found in any other system) to yield the observed hydrogenation rates. Furthermore, if impurities were the source of the activity induced by spillover, why is there an optimum in the pretreatment temperature? The impurities would still exist after higher temperatures of pretreatment (unless they are volatile). The most consistent interpretation of these observations is that the silica has been activated by the spiltover hydrogen and not that some undetectable impurities are the source of the observed activity.

posure to spiltover hydrogen were found to be important activation parameters. The rate (per gram) and the activation energy for ethylene hydrogenation varied as these parameters were changed. Experiments 1–4, 7, and 9–11 were used to estimate the rate while experiments 2–8 were used to estimate the apparent activation energies. The evacuation times and temperatures for the majority of the experiments were 8 h at ~430°C. The effect of varying the time and temperature of evacuation is seen in the last eight experiments. Interestingly, we found no effect of the hydrogen pressure used in the activation processes.

RESULTS AND DISCUSSION

The reaction rates are compared based on a calculated turnover frequency. The calculations depend on an estimated concentration of active sites. The standard reaction conditions involved a 10 : 1 hydrogen (or deuterium)-to-ethylene ratio at around 550 Torr with reaction at 200°C. Initially the number of sites created was estimated by ethylene adsorption at the reaction temperature (200°C). This assumes that the ethylene saturates the active sites created on the silica. This was assumed as the reaction is effectively zero order in ethylene. The calculated $\sim 10^{12}$ sites/cm^2 is generally consistent with earlier estimates (see above).

Blank Studies

Several blank runs were performed. As an example the evacuation and exposure to hydrogen were performed without the source of spillover present in the reactor. Following this treatment, ethylene is not adsorbed and there is no hydrogenation and only slight H_2–D_2 exchange at 200°C. The source of spillover is necessary for the induction of any measurable activity. In experiment 7 all other conditions were similar except that the silica and Pt were only exposed to hydrogen for 6 h. Again no ethylene adsorption or hydrogenation activity was found. However, in this case (with contact) considerable hydrogen adsorption is known to take place (to $>10^{12}$/cm^2). Catalytic activity requires a long period of pretreatment, possibly because there was no direct contact between the source of spillover and the silica. Interestingly, when the bucket was relowered onto the silica and exposed to hydrogen for an additional 8 h (experiment 7A), hydrogenation activity was induced.

During the blank studies little water was detected (by mass spectrometry) in the gas phase during the evacuation or activation steps; i.e., the amounts vary from undetectable to the equivalent of 4×10^4 molecules/cm^2 at high temperatures (to 460°C) or for long evacuation times (12 h). This was not the case if there was contact between the source of spillover and the silica for longer times. The relationship between water formation and activity will be discussed below.

Gas-Phase Products from Activation

In addition to adsorption onto the surface of oxides there is a possibility that spiltover hydrogen is able to react with other adsorbed species or with the oxide surface. As these products may be involved in the creation of active sites an on-line mass spectrometer was used to analyze the gas phase after the activation step. During the initial activation studies, gas-phase products such as water and methane were observed, although they were not consistently recorded. These products were not detected after the evacuation or in the gaseous hydrogen prior to exposure to the source of spillover and silica. It became apparent that the quantification of these products might provide valuable insight into the process of activation.

There is no notable difference ($5.7 \pm 3 \times 10^{12}$/cm^2 of silica surface) between the amounts of ethylene adsorbed for the various experiments, whereas the catalytic activity differs significantly depending on the conditions of pretreatment of the samples. The adsorption of ethylene seems to be a qualitative but not a quantitative measure of activity. It seems to reflect the total number of potentially active sites (see above) but not the actual concentration of active sites; however, this will be used below to initially estimate the TOFs for ethylene hydrogenation.

The quantity of methane formed during the standard activation procedure gives an average of 4×10^{12} molecules formed for each square centimeter of silica surface. Again the quantity of methane formed seems independent of the time of pretreatment and, at best, a weak function of the reduction temperature. The source of the carbon giving rise to the methane formation is not known. As the stopcock grease used in the system is hydrocarbon based (i.e., Apiezon H), this could have been the source of carbon. However, for two experiments, Dow Corning high-vacuum silicon grease was substituted on the key joints adjoining the reactor in the system and there was no difference in the production of methane. We conclude that the stopcock grease was not the source of the methane. Another possible source of the methane was from the hydrocarbon species already present on the Pt/alumina. However, in two experiments we reused the same platinum-containing sources of spillover and there was no substantial difference in the amount of methane formed.

The carbon seems to be present on the silica Aerosil. In several experiments deuterium was used during the activation process, and CD_4 and HDO were the dominant gaseous products. This implies that methoxyl groups, possibly present on the silica, are not involved, as CH_3D should have been the initial product. The carbon is probably present as organic impurities left from preparation or storage. High-temperature pretreatment may form a carbonaceous residue on the silica that is removed by the spiltover hydrogen (as in carbon gasification (*22–24*)). In contrast, the formation of water during the activation is noticeably affected by differences in the activation conditions. The selective production of HDO suggests that the surface is being dehydroxylated by atomic deuterium (spiltover) during the activation process.

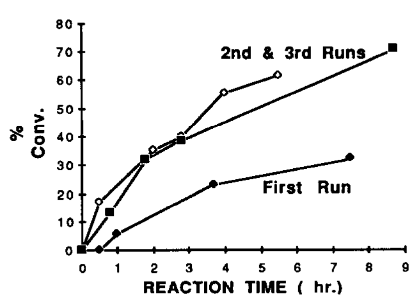

FIG. 1. Typical conversion vs time for ethylene hydrogenation at 200°C following activation of silica by spiltover hydrogen.

TOF for Ethylene Hydrogenation

Typical ethylene conversion as a function of time for experiments which correspond to 10 h of exposure to spiltover hydrogen at ~430°C following 8 h of evacuation at 422°C (experiment 2) is shown in Fig. 1. An induction period is evident for the first run following activation. Subsequent hydrogenation runs over the same activated silicas do not have an induction period.

A concentration of 10^{12} sites/cm^2 was initially assumed to estimate the turnover frequency for ethylene hydrogenation at 200°C. (Note a more consistent basis for estimating the concentration of active sites has been deduced in these studies as discussed below). The influence of the time of exposure to hydrogen at 430°C on the activity for several runs is shown in Fig. 2. The silica does not instantaneously become active; at least 7 h is required for this experimental configuration before the onset of hydrogenation activity is evident.

The TOFs shown in Fig. 2 are based on an estimated active site concentration found under optimum conditions. We do not believe that the actual turnover frequency is changing but, more probably, that the actual number of active sites is in-

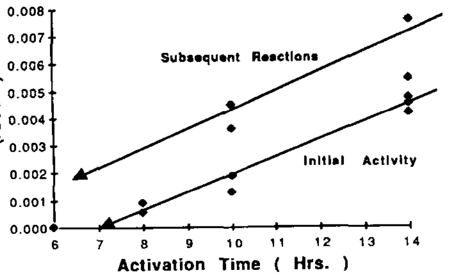

FIG. 2. Estimated initial and subsequent turnover frequencies (based on ethylene adsorption) for ethylene hydrogenation at 200°C as a function of the time of exposure to spiltover hydrogen.

creasing for longer times of exposure to spiltover hydrogen (see below).

The effect of the temperature of exposure to spiltover hydrogen (activation) is depicted in Fig. 3. There is an apparent difference due to the times of evacuation prior to the exposure to spiltover hydrogen. Evacuation times of 8 (lower curve) and 12 or more hours are represented. Both times of evacuation induce hydrogenation activity onto the silica. For activation by spiltover hydrogen at least 12 h of evacuation is required to achieve maximum activity between 400 and 460°C. Above 480°C hydrogen spillover is not able to induce appreciable hydrogenation activity. The activation process is not controlled solely by the "kinetics," i.e., longer times of exposure to spiltover hydrogen *cannot necessarily* compensate for lower activation temperatures. We conclude that the state of the surface (in particular, the nature of the hydroxyls) controls the maximum concentration of active sites that may be produced. The rate of creation of active sites is dictated by the concentration of these "precursor sites," the availability of spiltover hydrogen, and the kinetics of the activation process. As studied in our experiments, the indirect contact between the source of spillover and the silica may accentuate the induction time for the creation of measurable activity. The creation of pathways between the phases (source to bucket to silica) may also require a period of time involving specific surface transformations.

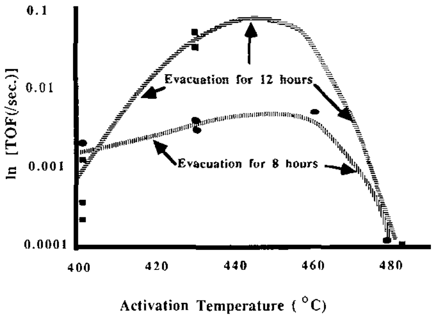

FIG. 3. Relationship between the estimated turnover frequencies (based on ethylene adsorption) for ethylene hydrogenation at 200°C as a function of the temperature of exposure to spiltover hydrogen. Prior to this "activation" at 430°C the samples were evacuated for either 12 or 8 h at 430°C.

The Production of Water and Active Sites

The mechanism by which active sites are created on silica by the reaction of spiltover hydrogen is complex. The most consistent picture that emerges is that active sites are created by the dehydroxylation of the silica surface with the concomitant production of water. As shown in Fig. 4, the amount of water produced depends on the temperatures and times of evacuation and activation of the silica. As the period of activation is increased from 8 to 12 h, the production

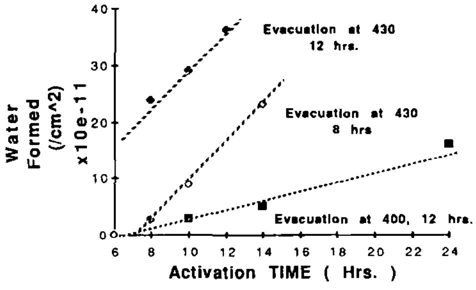

FIG. 4. Water formation expressed as a concentration per area of silica surface as a function of the time of exposure to spiltover hydrogen. Differing lines correspond to different pretreatment (evacuation times and temperatures) conditions.

of water increases. As the temperature of activation is increased (up to 12 h following 8 h of evacuation) the amount of water produced increases. If the silica is first evacuated above 500°C, hydrogen spilled over at lower temperatures does not produce any additional water and there is no significant hydrogenation activity.

One complexity in the relationship between water production and the induction of catalytic activity comes from the "induction period" required for the creation of activity and the production of water during the exposure to hydrogen. Even after the source of spillover (and the silica) has been exposed to hydrogen for up to 6 h, negligible water was produced and no measurable hydrogenation activity was induced on the subsequently isolated silica. Instead, both the activity and the water production increased almost linearly with exposure time after this initial period. As alluded to above, the indirect contact between the source of spillover and the silica may give rise to this "induction period" for the activation process since the hydrogen transport from the platinum across several interfaces (including the fritted-glass bucket) and onto the silica may take time to be established initially. If the induction period were due to a slow controlling transport, the overall rate would be limited by this transport throughout the activation process. Furthermore, the period of induction depends on the time of calcination prior to activation (all other conditions constant). Following an 8-h evacuation there is a 7-h period before water is produced; however, less time elapses before water is evident if the sample is evacuated for longer time periods. Possibly the creation of "bridges" across the interfaces may be initiated during this high-temperature evacuation. The results do not provide any more specific insight into these secondary processes.

The connection between the production of water and the creation of active sites on the silica is strengthened by plotting the reaction rate (expressed as the calculated TOF based on an assumed constant density of active sites) against the water produced. This is shown in Fig. 5 for samples that had been evacuated at 430°C for 8 h. The somewhat linear relationship between the activity and the production of water leads us to conclude that the reaction between the spiltover hydrogen and the surface hydroxyls gives rise to the production of H_2O (or HDO if deuterium is spiltover, see above) which occurs with the creation of active sites. Differences in activity would therefore be due to differences in the number of active sites instead of differences in their specific activities.

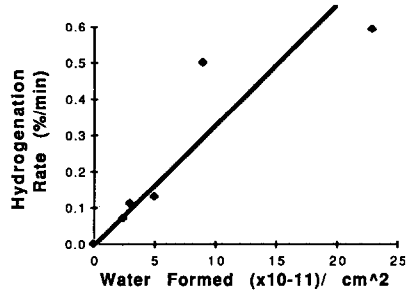

FIG. 5. Relationship between the relative rate for ethylene hydrogenation and the amount of water formed (expressed per cm^2 of silica surface × 10^{-11}) during the exposure to spiltover hydrogen.

ANALYSIS

Based on the activation results, the rate of production of active sites can be expressed as an irreversible reaction with a rate, R_a, that is proportional to the concentration of spiltover hydrogen, H_{sp}, and the concentration of reactive hydroxyls, SiOH* (probably "associated"), viz., $R_a = k_a[\mathrm{SiOH}^*]^i[\mathrm{H}_{sp}]^j$, for a rate constant k_a and exponents i and j (probably 1). Only about 1% of the 10^{14} hydroxyls/cm^2 (*2–4*) are able to react to give rise to active hydrogenation sites. As the surface concentration of spiltover hydrogen and surface hydroxyls was not determined prior to each activation, the exponential dependencies were not estimated.

The turnover frequency for ethylene hy-

TABLE 2

Relative Activity Calculated Based on either Ethylene Adsorption or Water Production during the Activation by Spillover (Each is Expressed per cm^2 of Silica Surface)

Run	Act. time (h)	Act. temp. (°C)	React. rate (%/min)	Water/cm^2 $(\times 10^{-11})$	TOF-W (s^{-1}) $\times 10^2$	Eth.-Ads./cm^2 $(\times 10^{-12})$	TOF-E (s^{-1}) $\times 10^2$
A	8	430	0.068	2.5 ± 1.5	0.34	3.8	0.052
B	10	430	0.5	9 ± 1.5	0.5	8.7	0.048
C	10	400	0.11	3 ± 2	0.38	8.0	0.101
D	14	430	0.59	23 ± 2	0.33	4.0	0.006
E	14	400	0.13	5 ± 2	0.38	NM[a]	—

Note. Ethylene hydrogenation was conducted for a 10 : 1 ethylene : hydrogen ratio of 200°C. TOF-W and TOF-E are the turnover frequencies based on the amounts of water produced during activation or the subsequent amounts of ethylene adsorbed on the silica, respectively.

[a] Not measured.

drogenation may be calculated based on the concentrations of active sites estimated by several approaches. Initially the active sites have been estimated by the amount of spiltover hydrogen. This gives a concentration of 10^{12}–10^{13}/cm^2. More directly the concentration of active sites might be calculated based on the amount of ethylene adsorption onto a surface exposed to spiltover hydrogen; again this is consistently between 10^{12} and 10^{13}/cm^2. Alternately, the concentration of active sites may be estimated from the amount of water produced during the (high-temperature) exposure to spiltover hydrogen. The relative activities and turnover frequencies based on these last two approaches are listed in Table 2. Each sample had been evacuated at 430°C for 8 h prior to activation.

The most consistent method of estimating the concentration of active sites and subsequently the turnover frequencies seems to be based on the water produced during activation. It should be noted that the conditions represented in Table 2 were not the optimum activation conditions that were found. At least 12 h of evacuation of the silica prior to activation is better. Furthermore an activation temperature between 430 and 460°C seems to be optimum. With these conditions the concentrations of active sites from each of the approaches discussed above are similar; i.e., each gives greater than 10^{12} but less than 10^{13} sites created per square centimeter of silica. The maximum TOFs estimated in prior studies (i.e., 10^{-1}/cm^2) is consistent for each approach; however, the calculations based on the water produced explain the greatly differing activity due to different pretreatment conditions. This conclusion is based on a presumption of similar specific activity on the active sites as contrasted with proposing sites with greatly varying specific activities.

The nature of the hydroxyls which serve as precursors of the active sites can be hypothesized. Pretreatment of the silica above 500°C precludes the induction of activity. Between 430 and 500°C the concentration of isolated hydroxyls decrease only slightly while the associated hydroxyls (vicinal and geminal which involve 10^{12}–10^{13}/cm^2 each (*2–4*)) decrease substantially. It seems that these associated hydroxyls are the precursors. However, as the concentration of active sites is a small fraction of the total hydroxyls (either isolated, associated *or* isolated), certain hydroxyls seem to be involved, possibly at edge or corner sites, or at other "stressed" sites. Both Peri (*2*), and Hockey and Pethica (*25*) have suggested the formation of "stressed" hydroxyl bridges on silica after treatment from 400 to 750°C; furthermore, they speculate that this is a result of proton migration on the silica. These more reactive hydroxyls may react with spiltover hydrogen to dehydroxylate the surface and produce water. Possibly both associated and stressed or stressed associated OHs are involved. Temperatures below 400°C do not create these stressed hydroxyls and yet associated hydroxyls are present at lower temperatures. At 430–460°C the rate by which they form requires 6–12 h. Above 500°C the associated hydroxyls are diminished whereas stressed *isolated* sites would still be present. By dehydroxylation an underlying silicon may simply be exposed and be part of the active sites that are created. The resultant activation would be similar to that proposed for other "basic" oxide surfaces. The presence of stressed oxide linkages and unique silicon environments giving rise to catalytic activity is known to be created with higher temperature pretreatment of silica (*26*).

Assuming that the water production corresponds to the production of active sites, one can calculate the activation energy for the creation of active sites (and water) from instantaneous rates of water production. The apparent activation energy for the activation of silica is calculated to be 28 kcal/g mol.

CONCLUSIONS

The induction of catalytic activity on silica seems to involve the dehydroxylation of the surface by reaction of specific hydroxyls with spiltover hydrogen. These specific hydroxyls seem to be "associated" (vicinal or geminal, as contrasted with isolated species) and may involve "stressed" sites. The product of the activation process is water. In excess of 10^{12} sites/cm^2 are created with an activation energy of 28 kcal/g mol. We suggest that the specific activity created on these sites is similar and estimate that the specific TOF for ethylene hydrogenation approaches 10^{-1}/s at 200°C. Differences in activity would be due to the efficiency of the activation processes creating more or fewer active sites. An induction period may exist for the activation process as an interface for the transport of spiltover hydrogen between the source of spillover and the activated surface may need to be developed. A similar mechanism may exist for other oxides activated by exposure to spiltover hydrogen.

ACKNOWLEDGMENTS

The authors greatly appreciate the support of the National Science Foundation, Grant CPE 82-21800, and the Petroleum Research Fund, Grant 13703-AC7, for this research. We also thank Analog Devices for their donation of computer equipment. We further thank S. Teichner, G. Pajonk, V. Haensel, E. L. Weist, and J. F. Cevallos-Candau for useful discussion on the interpretation of these results.

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