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Thermal Activation of Silica at Temperatures below 500°C

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A simple low-temperature treatment (below 500°C) of several types of silica was found to induce catalytic activity toward hydrogen–deuterium exchange, the degree of which was measured with a pulse-flow microreactor. Silica samples were heated in a microreactor in the presence of an argon carrier gas. Pulses of hydrogen and deuterium gas mixtures were injected into the flow and the effluent stream was monitored for H_2, D_2, and HD. In some cases equilibrium amounts of the effluent gases were observed. Activation of the silicas appeared to be related to the dehydration of the silica surfaces. After activation, the surface of one of the silicas, Cabosil M5, was found to catalyze the hydrogenation of ethylene to ethane and to catalyze extensive exchange when deuterium was used as the hydrogenation reagent. © 1994 Academic Press, Inc.

INTRODUCTION

We are reporting a simple and heretofore unreported low-temperature activation (below 500°C) of silica toward hydrogen–deuterium exchange. The same activated silica demonstrated catalytic activity toward the hydrogenation of ethene. Previous work, primarily by Low and co-workers, has shown that chemically modified silicas could be converted into "reactive silica" by treatment at very high temperatures (600–900°C) under high-vacuum conditions for extended periods (1). The characteristics of the resulting "reactive silica" produced under Low and coworkers' conditions differ widely from those in the work presented here both in chemisorptive ability and in catalytic activity. Other workers have shown that a hydrogen spillover mechanism may render silica surfaces active toward hydrogenation reactions (2–4). In each of those studies, the activity was interpreted as the result of the spillover of hydrogen from the noble metal surface onto the silica. In one study, the activity of the silica surface was retained after the metal was removed (4). The results of our current investigation show that certain silica surfaces can be made catalytically active toward hydrogen–deuterium exchange and toward hydrogenation of ethene without the use of a noble metal, without extreme temperatures, and without chemical modification of the silica.

Specifically, a simple thermal treatment to 320°C for 16 h of a silica (Cabosil M5, 200 m^2/g),[1] in a flowing stream of argon, was sufficient to activate the silica surface. Once activated thermally, the silica rapidly converted equimolar mixtures of hydrogen and deuterium gas to mixtures of hydrogen, deuterium, and hydrogen deuteride (HD) at near-equilibrium values. In addition, mixtures of ethene and hydrogen in an argon carrier produced significant amounts of ethane on this activated silica surface.

EXPERIMENTAL

Apparatus

All of the studies reported in this paper were carried out in a pulse-flow microreactor of a very simple design that has been previously described (5). In this study, the original design was slightly modified in that the stainless-steel reactor was replaced by a cylindrical Vycor tube (150 mm × 14 mm o.d.) with Teflon endcaps connected to the gas manifold system (Fig. 1). The temperature of the reactor was maintained by a thermostatically controlled oven. A flow of carrier gas, typically argon, was maintained at 4.0 ml/min unless otherwise specified. The gas manifold on the upstream side of the reactor allowed pulses of hydrogen, deuterium, or other gases to be injected into the argon stream which then passed through the reactor. The effluent stream from the reactor was sampled continuously via a capillary tube to the inlet of a quadrupole mass spectrometer (Ametek MA100M). Typically the intensities (ion counts) of H_2, HD, and D_2 were monitored simultaneously as a function of time. Quantitative data were obtained by calibration using pulses of known amounts of gases. Areas under the envelope of the intensity-versus-time plots produced by the pulses showed a linear relationship to the number of moles of gas pulsed.

For many of the experiments, simultaneous pulses of two different gases were injected into the carrier stream

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[1] Reference to brand names is to facilitate understanding and not meant to imply endorsement by the U.S. Department of Energy.

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within 15 s of each other. Since the observed peak width at half-height in the intensity-versus-time output produced by the mass spectrometer is about 3 min, the resultant areas of simultaneous pulses overlap to greater than 95%. Figure 2 shows simultaneous pulses of hydrogen and deuterium gases at 150°C in (a) an empty reactor and (b) a reactor containing 1.00 g of an activated silica (Cabosil M5).

Thermal gravimetric analyses were performed on selected silica samples on a Perkin–Elmer TGA-7 apparatus, operating over a temperature range from 40.0 to 700°C, typically at a heating rate of 10.0°C/min. Samples treated in such manner normally showed an initial rapid loss in weight of 1.8–2.0% from 40.0 to 100°C, followed by a plateau region with minimal loss of weight (100 to 150°C), and then slow loss of up to an additional 2.0% during the remainder of the heating period to 700°C.

Sample Preparation

Silica samples were generally kept at room temperature under air in a closed container. The only pretreatment, other than that described for each individual experiment, was drying at 120°C for 2–4 h, *in situ*, with an argon flow. The silica samples, Cabosil M5 and Cabosil HS5, were purchased from the Cabot Corporation. Other silicas used in this study were a Pyrex wool (Corning 3950), a quartz wool (Leco 501-608), and a commerical grade of silica, "Sea Sand" (Fisher S-25). The silica samples were used "as received" with two notable exceptions. In one case, a 1.00-g sample of Cabosil M5 was washed with 100 ml of methanol, filtered, and rotovapped to dryness at 60°C under vacuum. In the second case, a 1.00-g sample of Cabosil M5 was washed with 100 ml of deionized water, filtered, and rotovapped to dryness at 60°C under vacuum. The behavior of each of these pretreated silicas was identical to that of the "as received" samples described in this paper. Elemental analysis of the Cabosil M5 fumed silica by spark source mass spectrometry showed the material to be of very high purity (>99.5%) with impurities of aluminum, copper, iron, magnesium, potassium, and sodium below the 5.0-ppm level and with calcium and chlorine at 12.7 and 35.5 ppm, respectively, as the major impurities.

RESULTS AND DISCUSSION

Hydrogen–Deuterium Exchange

When a 1.00-g sample of silica (Cabosil M5, 200 m^2/g) was placed in the reactor and heated for 16 h at 320°C in an argon flow (4.00 ml/min), the sample became catalytically active toward hydrogen–deuterium exchange as well as toward hydrogenation of ethene gas. Simultaneous pulses (see Experimental) of hydrogen and deuterium gases into the argon stream at 320°C produced a mixture containing a significant quantity of hydrogen deuteride gas as well as both hydrogen and deuterium gases (Fig. 2B). The number of moles of each of these gases was determined from the integrals of the respective intensity-versus-time curves. Calculation of the reaction quotient Q ($Q = [HD]^2/[H_2][D_2]$) for this set of data results in a value of 3.5. Comparison of this value with the known values (6, 7) for K_{eq}, which increase from 3.3 at 25°C to 3.9 at 400°C, indicates that equilibrium had essentially been achieved. Prior to heating the sample, no activity was observed and no activity was observed until the temperature exceeded 150°C. On heating above 150°C, the activity increased very slowly. To activate the silica quickly (in less than 30 h), temperatures in excess of 250°C were needed (see further details below). Additionally, an empty reactor treated for 16 h at 320°C showed no production of HD when simultaneous pulses of hydrogen and deuterium were introduced (Fig. 2A). Thus, the presence of an activated silica must be responsible for the production of HD in the former experiment.

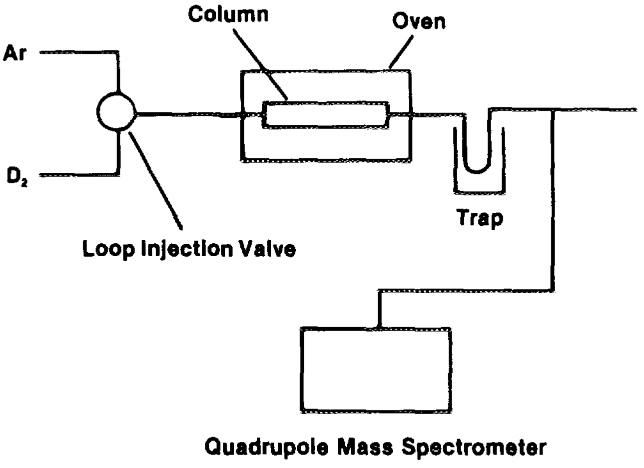

FIG. 1. Schematic of the pulse-flow microreactor.

Once activated, the silica maintained its ability to promote exchange at lower temperatures. For example, after activation at 320°C, the production of equilibrium amounts of H_2, HD, and D_2 was still observed on lowering the temperature to 203°C (Q = 3.5). In fact, equilibrium quantities of the three gases were produced at temperatures as low as 120°C (Q = 3.4). Not until the temperature was lowered to 70°C did the rate of production of HD fall off appreciably (Q = 2.6). However, when the temperature was returned to 203°C, equilibrium amounts of the three gases were produced once again (Q = 3.5).

Ethene Hydrogenation

Hydrogenation activity was explored in two separate experiments. First, a sample of silica (Cabosil M5), activated at 320°C for 16 h under argon flow, was cooled to 151°C. Simultaneous pulses of ethene and hydrogen were passed through the sample using argon as the carrier. A mass spectral response showed a mixture of both ethene and the expected hydrogenated product, ethane. From the intensities of the mass spectral peaks at *m/e* 28, 29, and 30 it was estimated that at least 50% of the ethene had been hydrogenated. Furthermore, simultaneous pulses of deuterium and ethene gave a complex pattern of peaks from *m/e* 28 to 35. This pattern was interpreted as the product of both deuterogenation and exchange reactions. The appearance of peaks from *m/e* 28 to 32 can be explained by the exchange of ethene. The peak at *m/e* 32 may also be due to deuterogenation of ethene to ethane-d_2. The higher masses (*m/e* = 33–35) indicate significant exchange on the ethane that forms by deuterogenation. Since this experiment used simultaneous pulses of deuterium and ethene in an argon flow, evidence for the complete exchange as well as deuterogenation producing a perdeutero-ethane was obscured by the overlap of the signal from the argon-36 isotope. However, perdeuteration yielding C_2D_6 on this silica was observed in flowing deuterium as discussed below. Pulses of ethene were completely hydrogenated by changing the flow of the carrier gas to hydrogen (3.0 ml/min). Comparison of the mass spectra of pulses of ethene in argon (Fig. 3A) and a pulse of ethene in hydrogen (Fig. 3B) clearly shows that the ethene was hydrogenated. In addition, comparison of Fig. 3B with the mass spectrum of an authentic sample of ethane shows that the ethene was completely hydrogenated. Evidence of a highly deuterated species including C_2D_6 (*m/e* = 36) was found (Fig. 3C) when a pulse of ethene was injected into a deuterium flow (3.0 ml/min). Thus the silica, activated simply by a thermal treatment at 320°C for 16h, catalyzed both the hydrogenation and deuterogenation (with extensive exchange) of a pulse of ethene at 151°C.

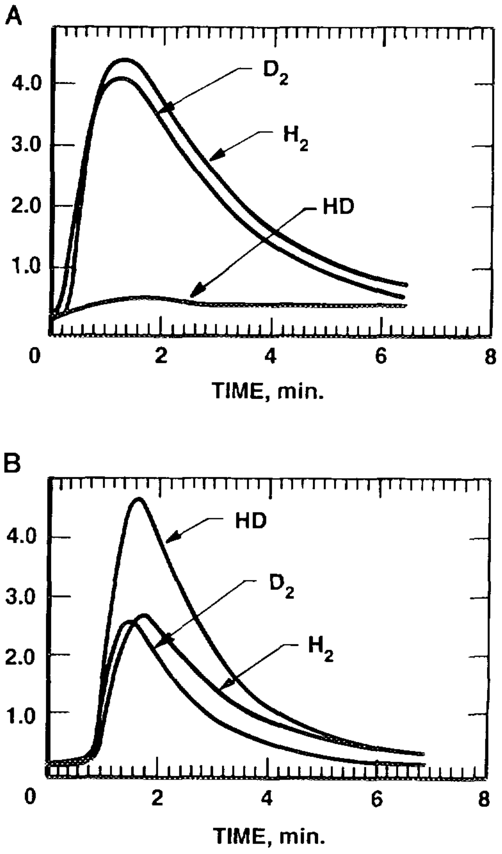

FIG. 2. Mass spectrometer response in the intensity-vs-time mode for simultaneous pulses of H_2 and D_2 in argon at 4.0 ml/min at 150°C in (A) an empty reactor and (B) a reactor containing 1.00 g of an activated silica (Cabosil M5).

Nature of the Activation Process

The requirements for activation of Cabosil M5 were explored by using different combinations of time, temperature, and flowing gases. Thus, active catalysts were also prepared by calcining Cabosil M5 in a flow of air at 500°C for 12 h, followed by a flow of hydrogen at 400°C for 0.5 h. Alternatively, treatment in hydrogen alone at 400°C for 12 h was also successful in activating the surface. After each of the activation sequences above, the same check for activity as used before, simultaneous pulses of hydrogen and deuterium in argon flow, was positive, giving equilibrium amounts of HD. Although heating in hydrogen does result in an active catalyst, it is clear that hydrogen flow is not a necessary condition for activation since heating with argon is equally effective in activating the surface. This is an important distinction between the present work and earlier reports of activation that are said to require the spillover of hydrogen (2–4).

The activated silica produced by low-temperature heating differed markedly from an active silica prepared by Low and co-workers (1). A "reactive silica," as termed by Low, was prepared from an Aerosil or Cabosil that was first methoxylated and then subjected to a high-temperature treatment (600–900°C) under vacuum. Treatment of the resulting "reactive silica" with hydrogen at temperatures less than 500°C converted it to a less active form, presumed to be a silyl hydride species. The more reactive form could be regenerated at high temperatures (600–900°C) under vacuum. Thus, the active sites created at high temperature were not active at temperatures below 500°C. Since all of our work was performed below 500°C, we conclude that the activity we see is clearly not due to the same kind of site that were responsible for activity reported in Low's "reactive silica."

A second major difference in the two active silicas is centered around the interaction of the active surface with ethene. Low's reactive silica chemisorbs ethene, apparently with some polymerization (1b), whereas our active silica simply returns ethane when ethene is pulsed into a hydrogen flow. However, it should be kept in mind that the manner in which the experiments were conducted (Low's static system vs our pulse system) was quite different.

In the present work, the temperature appeared to be the only contributor to the activation of the surface. After several activating temperatures were tried, it was found that Cabosil M5 could be activated in argon flow at temperatures as low as 250°C. However, longer times (72 h) were necessary at this lower temperature. Almost no activity could be detected after treatment in argon flow for a week at 150°C. This establishes a practical threshold for an activation temperature of somewhere between 150 and 250°C.

It is generally accepted that both physically adsorbed water and chemically produced water are released when silicas are heated. Chemical release may be a result of dehydration of adjacent silanol hydroxyls producing a siloxyl-type bridge, Si–O–Si (8). Perhaps dehydration of geminal disilanols, HO–Si–OH, is possible but high concentrations of these groups in the silicas studied here have not been reported to date. Physically adsorbed water can be released at temperatures between 50° and 150°C. It appears that removal of physically adsorbed water is not sufficient for the activation of silica since no activity was evident after heating at or below 150°C. The necessity of heating to temperatures above 150°C points to the dehydration of adjacent silanols as a crucial step in the activation. Water production was observed concomitant with an increase in activity when the samples were heated to these higher temperatures. As shown above, once activated, the surface may be cooled to temperatures as low as 70°C and hydrogen–deuterium exchange is still observed. Thus, high temperature is not required for the exchange itself, only for the activation of the surface.

The thermal analysis is also consistent with the above observations. As the Cabosil M5 is heated at a constant rate of 10.0°C/min, the initial rapid loss of weight (1.8–2.0%) is presumably due to the loss of the physically adsorbed water. Most of this is released in the first 8 to 10 min as the sample is heated to just over 100°C. After this initial release, the sample weight remains essentially constant until the temperature has exceeded 200°C. Then, a slow but significant loss (up to an additional 2.0%) is observed on heating to 700°C. This loss of weight at the higher temperatures parallels that seen in our microreactor experiments described above where we observed water being released from Cabosil M5 at these elevated temperatures. In summary, the thermal analysis and microreactor experiments both support the conclusion that surface is being dehydrated by the condensation of adjacent silanols.

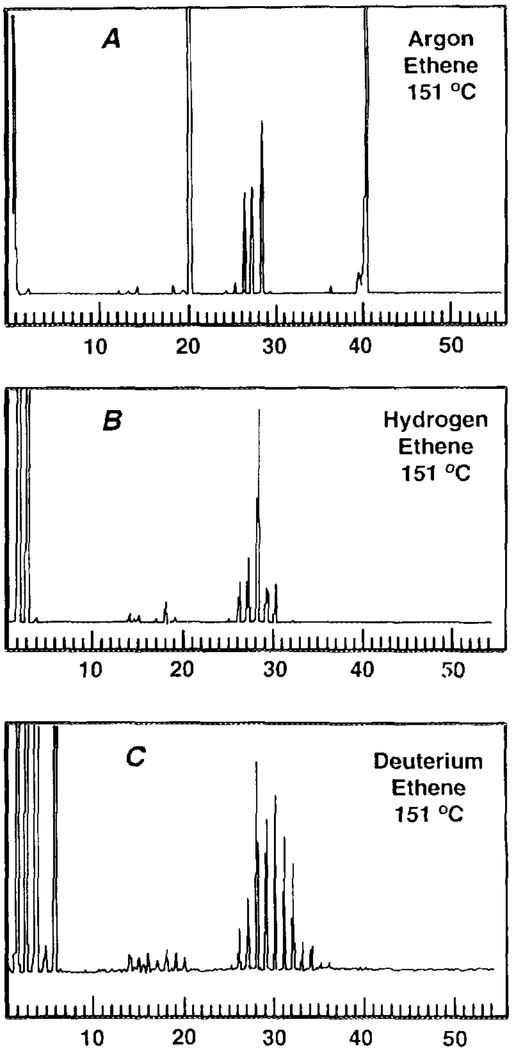

FIG. 3. Mass spectrum (intensity vs mass) resulting from the return of a pulse of ethene on activated Cabosil M5 at 151°C as a function of carrier gas: (A) argon, 3.0 ml/min; (B) hydrogen, 4.0 ml/min; (C) deuterium, 4.0 ml/min.

That the activity of the surface is related to its degree of hydration was confirmed in the following experiment. The thermally activated sample (Cabosil M5) was cooled to 115°C and a 10-μl injection of water was introduced into the argon flow just upstream of the reactor. The argon stream, now saturated with water, was allowed to pass through the reactor. Within 10 min at 115°C, the silica was no longer active toward hydrogen–deuterium exchange. Once deactivated in this manner, the silica remained inactive at 115°C. The sample could be maintained at this temperature for days without the return of activity, but thermal treatment at 320°C for 16 h restored the activity. The reversibility of the activation process is consistent with the interpretation that hydration/dehydration of adjacent silanols is an important step in the activation of the surface rather than simply physical adsorption/desorption of water on the surface.

Further studies are needed to determine how the dehydration of the silanols leads to the activation of the surface. At present, it is certain that the observation of catalytic activity is not limited to Cabosil M5. A preliminary survey reveals that many other silica surfaces can also be activated toward hydrogen–deuterium exchange by a simple thermal treatment (320°C for 16 h). These include a higher-surface-area Cabosil HS5 (325 m^2/g), ordinary pyrex wool (Corning 3950), and a quartz wool (Leco 501-608). We have seen a very minimal activity of the quartz reactor tube itself and a slight activity of a commerical grade of silica, "Sea Sand" (Fisher S-25), under identical activation conditions.

CONCLUSIONS

Clearly, these observations demonstrate that a low-temperature treatment may render silica catalytically active toward hydrogen–deuterium exchange and toward hydrogenation reactions. The activity obtained by thermal treatment is similar to that reported for the activation of silica surfaces by hydrogen spillover (2–4), but differs markedly from that seen by chemical modification and high-temperature activation (1). The activation of the silica in the present study required neither a noble metal, nor hydrogen gas, nor temperatures in excess of 500°C. The resulting catalytically active material in our work did not chemisorb hydrogen and moreover remained active in the presence of flowing hydrogen gas at temperatures well below 500°C. Also, in the present work, activation was found to be reversible through hydration/dehydration cycles. It appears that the degree of hydration of the surface plays a critical role in the activity. It is also pertinent to note that washing of Cabosil M5 with either methanol or deionized water does not remove its capacity to be activated. This observation along with the fact that similar activity is found with a number of different silica samples is strong evidence that the catalytic agent is indeed the silica surface and not a trace impurity to be found in a single sample. We are currently investigating the nature of the activation process and the extension of the work to these other silica surfaces.

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